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Sulfate and Particulate Emissions from In-Use Catalyst Vehicles: Regulated/Unregulated Emissions and Fuel Economy

New York State Dept. of Environmental Conservation, Albany

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Dec 79

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16. ABSTRACT

An emissions and fuel economy study of 56 catalyst cars in consumer use and maintenance has been performed by repeated testing of the cars over a two and one-half year period. This report summarizes analyses of the data base, and includes results on idle CO levels, mass emissions of HC, CO, NO_x, sulfate, SO_2 and total particulate; total particulate elemental analyses, catalyst activity, and fuel economy. Test cycles used were the 1975 FTP, one-hour 50 mph cruise, Congested Freeway Driving Schedule, Highway Fuel Economy Test, and idle,30 and 50 mph cruise for catalyst activity tests. Fuel economy data for over-the-road driving are also presented from on-board totalizing fuel and engine hour meters on each car.

Idle CO indicative of maladjusted carburetors (> 1%) was found to correlate with FTP CO emissions, purge of stored sulfur in the form of SO_2 from catalysts, and decreases in catalyst activity at idle in comparison to 30 and 50 mph activity results. Particulate sulfur emissions accounted for only 3.7% of fuel sulfur for the 256 CFDS tests in the data base. Over-the-road fuel economy was most closely represented by the FTP (city) value.

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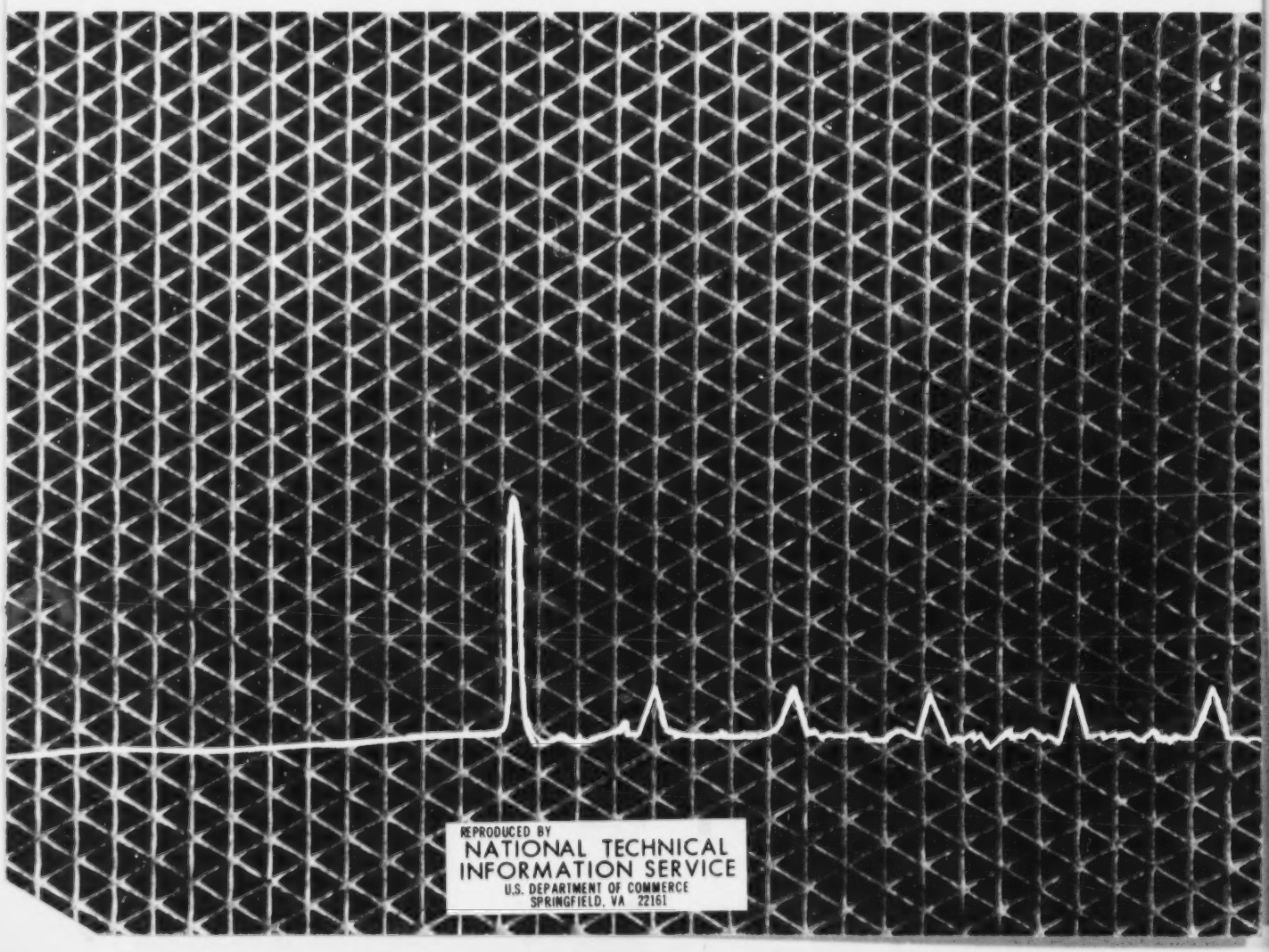

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EPA-600/9-79-047

December 1979

Sulfate and Particulate Emissions From In-Use Catalyst Vehicles: Regulated/Unregulated Emissions and Fuel Economy

by

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Prepared for

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Office of Research and Development
Office of Health and Environmental Assessment
Environmental Criteria and Assessment Office
Research Triangle Park, NC 27711

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FOREWORD

To assess the effects of pollution on the environment and the public health, a broad range of scientific and technical information is needed. This means that the Environmental Protection Agency must carry out activities simultaneously on several fronts, including the measurement, analysis, and precise characterization of the pollutants invading the environment, as well as the evaluation of the varied and often complex biological effects of these pollutants. By critically reviewing and interpreting such information, the Environmental Criteria and Assessment Office of EPA provides a scientific basis for decisions on the regulation of pollutants that may affect the environment or the public health.

This report presents the results of a study on the pollutant emissions and fuel economy of selected cars over a two and one-half year period. In focusing on catalyst-equipped vehicles operated under "real world" conditions, this study attempts to provide information needed to accurately assess a number of pollution problems associated with the use of automobiles.

Lester D. Grant
Director
Environmental Criteria and
Assessment Office

ABSTRACT

An emissions and fuel economy study of 56 catalyst cars in consumer use and maintenance has been performed by repeated testing of the cars over a two and one-half year period. This report summarizes analyses of the data base, and includes results on idle CO levels, mass emissions of HC, CO, NO_x, sulfate, SO_2 and total particulate; total particulate elemental analyses, catalyst activity, and fuel economy. Test cycles used were the 1975 FTP, one-hour 50 mph cruise, Congested Freeway Driving Schedule, Highway Fuel Economy Test, and idle, 30 and 50 mph cruise for catalyst activity tests. Fuel economy data for over-the-road driving are also presented from on-board totalizing fuel and engine hour meters on each car.

Idle CO indicative of maladjusted carburetors (> 1%) was found to correlate with FTP CO emissions, purge of stored sulfur in the form of SO_2 from catalysts, and decreases in catalyst activity at idle in comparison to 30 and 50 mph activity results. Particulate sulfate emissions accounted for only 3.7% of fuel sulfur for the 256 CFDS tests in the data base. Over-the-road fuel economy was most closely represented by the FTP (city) value.

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LIST OF ABBREVIATIONS

FTP	-- (1975) Federal Test Procedure
CFDS	-- Congested Freeway Driving Schedule, also known as S-7, SET-7, CUE
HFET	-- Highway Fuel Economy Test
OTR	-- Over-the-road
CVS	-- Constant volume sampler
XRF	-- x-ray fluorescence
BCA	-- Barium chloranilate
k	-- thousand (as in 5k miles = 5,000 miles)
IC	-- Ion Chromatograph
AEL	-- Automotive Emissions Laboratory, NYS Dept. of Environmental Conservation, Latham, NY
CID	-- Cubic inch displacement
S	-- sulfur
mi	-- mile(s)
hr	-- hour(s)
km	-- kilometer
g	-- gram
mg	-- milligram
µg	-- micro gram
mpg	-- miles per gallon
l	-- liter
mm	-- millimeter
nm	-- nanometer

CONVERSIONS

to convert from	to	multiply first column unit by
mi	km	1.6
mi/hr	km/hr	1.6
g/mi	g/km	0.625
mg/mi	mg/km	0.625
mpg	km/l	0.421
gm/gal	gm/l	0.264

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SECTION 1

INTRODUCTION

BACKGROUND

In 1974 and 1975 several engine stand and prototype vehicle studies[1-8] demonstrated the potential of catalyst equipped cars to emit sulfuric acid (sulfate) aerosol at sufficient levels to be of identifiable concern. As the manufacturing commitments to oxidative catalyst emission control technology were made well in advance of these findings, the need for a sulfate emissions data base from assembly-line produced, consumer-driven and consumer-maintained vehicles was evident. Sulfate emissions data for this purpose were part of a more comprehensive investigation of in-use catalyst cars summarized in this project report. While this work was in progress much of the concern for vehicular sulfate emissions lessened, mostly in response to the low emission rates found, especially from non-air pump catalyst cars[9-12]. In the present study, a group of vehicles were repeatedly tested over a period of two and a half years to characterize sulfate emissions, HC/CO/NO_x emissions under different test modes, idle HC/CO levels, fuel economy in laboratory and over-the-road (OTR) driving, catalyst activity, purge of stored sulfur from catalysts, particulate emissions, state of engine tune, and tank fuel characteristics.

The collection of field-service vehicular data is usually more time-consuming, cumbersome and expensive than permitted or warranted by the demands of time and the many questions for which data are needed. However, emission and fuel economy characteristics of consumer-driven and maintained vehicles relate directly to air pollution and energy consumption in general, and projections for the vehicle population at large are not always accurate if based on results from prototype vehicles. Within limitations, this project's data base should be useful for a variety of emission and fuel economy evaluations for first generation catalyst cars.

VEHICLE TESTING METHODOLOGY

A vehicle test protocol was adopted in response to specific data elements considered essential to the study. Vehicles were tested in "as-received" condition upon delivery to the New York State Department of Environmental Conservation Automotive Emissions Laboratory (AEL). Numerous engine parameters and idle HC/CO exhaust levels were logged, and a tank fuel sample was collected in preparation for dynamometer testing. HC/CO/NO_x emissions were measured by the 1975 Federal Test Procedure (FTP)[13] applicable to these cars.

A one hour 50 mph steady cruise test was included to: 1) collect particulate for 10 elemental analyses by x-ray fluorescence (XRF); 2) pre-condition the vehicle's catalyst for subsequent sulfate measurements during the Congested Freeway Driving Schedule (CFDS)[14]; and 3) provide a comparison of sulfate emissions between 50 mph cruise and the CFDS. Five successive CFDS test cycles were adopted to insure stabilized sulfate emission rates, since sulfur storage/release from catalysts had been identified as causing observations of erratic values of tailpipe sulfate emissions for successive test cycles (2,15-17). At the last vehicle test catalyst activity for HC and CO conversion was measured by sampling raw exhaust before and after the catalyst at idle, 30 mph and 50 mph.

Fuel economy was measured in all dynamometer test modes by carbon balance procedure. In addition, each vehicle was equipped with an engine hour meter and totalizing fuel meter throughout the project to provide over-the-road average speed and fuel economy between tests. Near the end of the project, a Highway Fuel Economy Test (HFET) was added to further characterize dynamometer fuel economy.

Test protocol and laboratory analyses procedures are covered in Section 8 in further detail.

VEHICLE TEST GROUP

Fifty-six 1975/76 model year catalyst-equipped cars made up the test group sample. Table 1 is a roster of these vehicles listing vehicle information and a "car number" identifier used throughout this report. Figure 1 is a mileage test point roster. While a total of 266 tests were performed, 10 tests were deleted as technically defective; therefore, 256 vehicle tests serve as the data base for this report.

Car #1 was stationed at AEL as a control vehicle and served as an overnight loan car in order to gain access to other test-group vehicles. It was fueled exclusively at AEL and maintained in accordance with manufacturer's specifications. The remainder of the test group vehicles were drawn from four institutional fleets in the Albany, N.Y. area and private vehicles accessed by letter solicitation to owners of all 1975/76 cars in the New York State Department of Environmental Conservation parking lot, 50 Wolf Road, Albany, N.Y. No screening criteria were used in establishing the test group. Private vehicle owners were provided a fill-up of gasoline and two car wash tickets as the only incentive for participation. Vehicle test and check-in results were provided to these owners only upon their request to minimize the influence of the testing program on these vehicles.

Table 2 provides a breakdown for 256 vehicle tests by vehicle manufacture, model year and ownership.

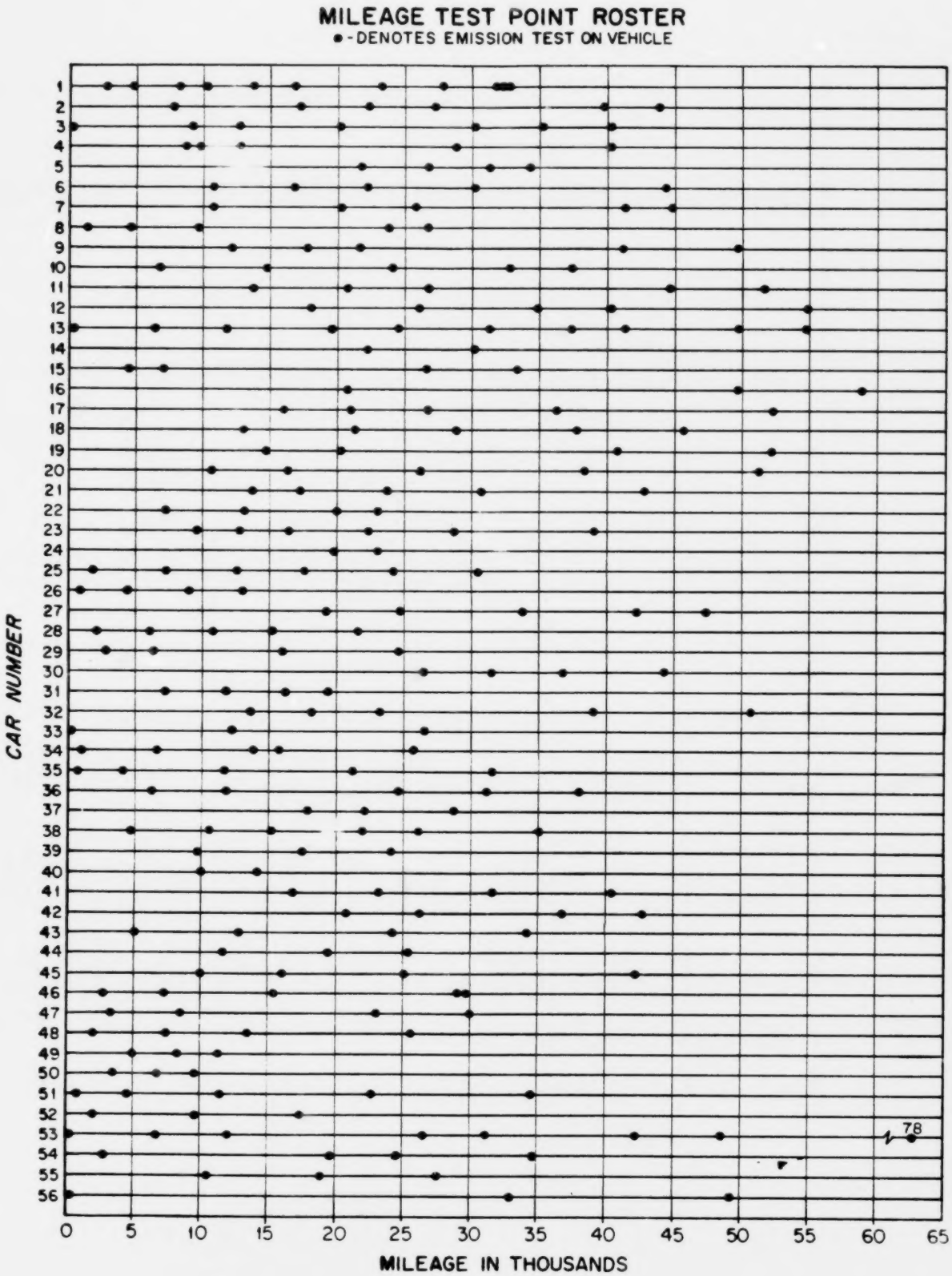
The test group is not statistically representative of the vehicle population at large. No particular attempt was made to accurately represent all makes, engine family types, inertia weight classes, etc. However, the test

Table 1

TEST GROUP ROSTER

Car No.	Year	Make	Model	Engine	Trans	Carb Vent.	Family	Air Pump	Cat. Type	Inertia Weight	Air Cond.
1	1975	Chevrolet	Bel Air Wagon	454-V8	A3	4	10-R4-3M	Y	B	5501	N
2	1976	Buick	Century Wagon	350-V8	A3	4	40J4	N	B	5000	Y
3	1975	Plymouth	Gran Fury	440-V8	A3	4	F-RB-HFC	N	M	5000	N
4	1975	Plymouth	Fury Wagon	318-V8	A3	2	F-LA2-6C	N	M	4500	N
5	1975	Dodge	Dart	225-I6	A3	1	F-RG-C2	N	M	3500	N
6	1976	Buick	Century Wagon	350-V8	A3	4	40J4	N	B	5000	Y
7	1975	Dodge	Dart	225-I6	A3	1	F-RG-C2	N	M	3500	N
8	1976	Mercury	Monarch	351-V8	A3	4	1-CEF	Y	M	4000	Y
9	1975	Plymouth	Fury Wagon	318-V8	A3	2	F-LA2-6C	N	M	4500	N
10	1975	Dodge	Dart	225-I6	A3	1	F-RG-C2	N	M	3500	N
11	1975	Dodge	Dart	225-I6	A3	1	F-RG-C2	N	M	3500	N
12	1975	Plymouth	Fury Wagon	318-V8	A3	2	F-LA2-6C	N	M	4500	N
13	1975	Plymouth	Gran Fury	440-V8	A3	4	F-RB-HFC	N	M	5000	N
14	1975	Ford	LTD	400-V8	A3	2	1CET	Y	M/N	5000	N
15	1975	Dodge	Coronet Wagon	318-V8	A3	2	F-LA2-6C	N	M	5000	N
16	1975	Dodge	Coronet Wagon	318-V8	A3	2	F-LA2-6C	N	M	5000	N
17	1976	Buick	Century Wagon	350-V8	A3	4	40J4	N	B	5000	Y
18	1975	Plymouth	Fury Wagon	318-V8	A3	2	F-LA2-6C	N	M	4500	N
19	1975	Plymouth	Fury Wagon	318-V8	A3	2	F-LA2-6C	N	M	4500	N
20	1975	Plymouth	Valiant	225-I6	A3	1	F-RG-C2	N	M	3500	N
21	1975	Plymouth	Valiant	225-I6	A3	1	F-RG-C2	N	M	3500	N
22	1976	Buick	Century	231-V6	A3	2	40E23	N	B	4000	Y
23	1975	Dodge	Dart	225-I6	A3	1	F-RG-C2	N	M	3500	N
24	1975	Mercury	Marquis	400-V8	A3	2	1CET	Y	M/N	5000	Y
25	1976	Ford	Pinto Wagon	140-I4	M4	2	2.3"A" 1CEF	Y	M	3000	N
26	1976	Ford	Elite	351-V8	A3	2	1CET	Y	M/N	5000	Y
27	1975	Chevrolet	Monza	262-V8	M4	2	10G23A	Y	B	3500	N
28	1976	Pontiac	Ventura	250-I6	A3	1	LK10F1	N	B	3500	N
29	1976	Chevrolet	Monza	140-I4	M5	2	10C2	N	B	3000	N
30	1975	Pontiac	Ventura	260-V8	A3	2	30H23E	N	B	4500	N
31	1975	Chevrolet	Chevelle	350-V8	A3	2	10J23	N	B	5000	Y
32	1975	Chevrolet	Monza	140-I4	M3	1	10C11	N	B	3000	Y
33	1976	AMC	Hornet	232-I6	A3	1	1	N	N	3500	N
34	1976	Plymouth	Fury Wagon	360-V8	A3	2	FD-360-2SS	N	M	5000	N
35	1976	Plymouth	Fury Wagon	360-V8	A3	2	FD-360-2SS	N	M	5000	N
36	1976	Plymouth	Volare	225-I6	A3	1	FD-225-1-5SS	N	M	3500	N
37	1975	Oldsmobile	Omega	250-I6	A3	1	10F13	N	B	4000	N
38	1976	Oldsmobile	Omega	260-V8	A3	2	30H2V	N	B	4000	N
39	1976	Oldsmobile	Cutlass	350-V8	A3	4	30J4	N	B	4500	Y
40	1975	Pontiac	Grand Prix	400-V8	A3	4	20K43	N	B	4500	N
41	1975	Pontiac	Astre	140-I4	A3	1	10C11	N	B	3000	N
42	1975	Chrysler	Cordoba	318-V8	A3	2	F-LA2-6C	N	M	4500	N
43	1976	Plymouth	Volare	225-I6	A3	2	FD-225-1-5SS	N	M	3500	N
44	1975	Mercury	Comet	250-I6	A3	1	250CAT/EGR Air(1CET)	Y	M	3500	N
45	1975	Ford	Gran Torino	351-V8	A3	2	351WCAT/EGR Air(1CET)	Y	M/N	4500	N
46	1976	Ford	Mustang II MPG	140-I4	A3	2	2.3 CAT/EGR Air(1CET)	Y	M	3000	N
47	1976	Ford	Torino	351-V8	A3	2	351WCAT/EGR Air"B"(1CET)	Y	M/N	4500	N
48	1976	Chevrolet	Chevette	97.6-I4	M4	1	10W1	N	B	2250	N
49	1976	Plymouth	Volare	225-I6	A3	1	FD-225-1-5SS	N	M	3500	N
50	1976	Cadillac	Coupe de Ville	500-V8	A3	4	KA60V4	N	B	5500	Y
51	1977	Buick	Century Wagon	350-V8	A3	4	740J4U	N	B	5000	Y
52	1976	Mercury	Monarch	250-I6	A3	1	1CEF	Y	M	4000	Y
53	1976	Plymouth	Gran Fury	440-V8	A3	4	FB-440-4HP-75	N	M	5000	N
54	1977	Buick	Century Wagon	350-V8	A3	4	740J4U	N	B	5000	Y
55	1976	Chevrolet	Impala	350-V8	A3	2	10J2	N	B	5000	N
56	1977	Plymouth	Gran Fury	440-V8	A3	4	FB-440-4HP-DE	N	M	5000	N

Figure 1


MILEAGE TEST POINT ROSTER
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MILEAGE IN THOUSANDS

group encountered "real-world" factors in much the same manner as the general vehicle population. This hypothesis is supported by the similarity of idle CO patterns in the test group to those from a larger sample of catalyst cars throughout New York State, tested as part of a 25,000 car, 5-year idle emissions inventory (11, 18).

TABLE 2. CLASSIFICATION OF CARS AND TESTS

	General Motors	Ford	Chrysler	AMC
56 Cars	21	10	24	1
29 Fleet Cars	6	2	20	1
26 Personal Cars	14	8	4	0
1 Control Car	1	0	0	0
1975 Model Cars	8	4	17	0
1976 Model Cars	11	6	6	1
1977 Model Cars	2	0	1	0
256 Emissions Tests	95	38	120	3
143 Fleet Tests	29	7	104	3
102 Private Tests	55	31	16	0
11 Control Tests	11	0	0	0

SECTION 2

CONCLUSIONS

SULFATE EMISSIONS

For 256 vehicle tests, CFDS sulfate emissions averaged 3.1 mg/mi, and only 14% of these tests gave sulfate emissions in excess of 10 mg/mi. These emission rates are significantly less than prototype results (1, 15, 16, 17) and are attributed to oxygen starvation of non-air pump catalyst systems with maladjusted carburetors. Another factor influencing these results was the low sulfur content of commercial unleaded gasoline used for testing (project average 0.020 wt % S).

FTP CARBON MONOXIDE EMISSIONS

CO was the most common pollutant outside the design standard for these vehicles, being greatly affected by maladjusted carburetors. Only 93 of 256 tests gave FTP CO at or below the 15 gm/mi standard. Idle CO level corresponded to FTP CO emissions. For the 116 tests characterized by idle CO less than 1% FTP CO emissions averaged 12.9 gm/mi, in contrast to the 140 tests on vehicles with idle CO greater than 1% which averaged 42.5 gm/mi FTP CO.

FUEL ECONOMY

Laboratory carbon balance fuel economy measurements showed close correspondence to EPA certification values applicable to test group vehicles. Fuel economy based on 1.5 million miles of over-the-road driving averaged about 10% higher than the measured FTP (city) values. Over-the-road vehicle speed averaged 33 mi/hr in contrast to 21 mi/hr for the FTP.

PURGE OF SO_2 FROM CATALYSTS

Catalysts stored sulfur in some operational modes, and released SO_2 upon deceleration to idle. This phenomenon was pronounced for vehicles with carburetors characterized by idle CO > 1%.

CATALYST CONVERSION ACTIVITY

Exhaust sampling before/after catalysts near the conclusion of the project showed 70% of the vehicles (30 out of 43) to be capable of 90% CO

and 75% HC conversions. Therefore, most tests in this project are considered to have been performed on vehicles with active catalysts.

Even active catalysts showed large decreases in CO conversion at idle if the carburetor was adjusted to give high engine-out CO (> 1%). This phenomenon results in dormant catalysts at times of high emissions, and also accounts for the observed decrease in CO emissions for cars restored to proper carburetor adjustment.

EMISSION TRENDS WITH MILEAGE ACCUMULATION

Emission rates of the measured pollutants were not found to be a consistent function of vehicle mileage.

SECTION 3

REGULATED AND SULFATE EMISSIONS

INTRODUCTION

No single method for organizing the data from these in-use vehicles has been found to be completely satisfactory. Instead, several different approaches have been included in this report in order to provide a composite picture of how various emissions related factors interrelate. In this section the data base has been analyzed by the following: 1) individual vehicle emissions averages; 2) mileage accumulation trends of the overall fleet; 3) individual vehicle mileage accumulation trends; and 4) tests grouped by various parameter subclassifications.

EMISSION RESULTS AVERAGED BY CAR

Emissions of each car, averaged over all tests on that car, are shown by car number in Table 3. The number of tests per vehicle and the mileage interval spanned from the first to last test are indicated for each vehicle. HC/CO/NO_x results are reported for the FTP, CFDS, and 50 mph cruise tests. CFDS values in Table 3 are taken from the second CFDS cycle, as discussed in Section 5.

EMISSION TRENDS WITH MILEAGE ACCUMULATION: OVERALL TEST GROUP

Changes in emissions with mileage accumulation for the test group were investigated by averaging all tests in the data base in 5,000 mile intervals (i.e. 0-5k, 5-10k miles, etc.). These results are shown in Table 4.

Individual columns in Table 4 show average emission rates for successive 5,000 mile intervals. Idle CO averaged 1.3% in the first interval, rose to 2.4% in the 5k to 10k mile interval and was relatively unchanged thereafter. The increase in FTP CO in the second 5,000 mile interval parallels the increase in idle CO. FTP HC emissions show an overall increasing trend with mileage accumulation. NO_x levels showed no significant change with mileage. Particulate sulfate emissions in both the 50 mph cruise and the CFDS show a significant falloff with increasing mileage.

Table 3. Average Emission Results by Car

CAR #	TESTS	MILES TESTED	IDLE CO %	FTP HC	FTP CO	FTP HOT CO(1)	FTP NOX	SC-C HC	SC-C CO	SC-C NOX	SC-C SO4	SC-C SO4(2)	CFDS HC	CFDS CO	CFDS NOX	CFDS SO4	CFDS SO4(2)
1	11	29376.6	0.01	0.77	21.28	1.36	1.93	0.02	0.01	1.38	9.75	14.44	0.08	1.18	1.94	9.81	14.50
2	6	36267.7	1.98	1.38	27.80	20.53	2.97	0.19	5.17	2.19	0.20	0.37	0.59	13.75	2.90	0.22	0.41
3	7	41869.1	3.73	2.27	56.79	42.93	2.69	0.03	0.07	2.79	3.33	5.39	0.55	15.71	3.16	1.37	2.68
4	5	31633.6	4.66	3.56	66.06	47.77	1.23	0.64	1.12	1.51	1.24	2.04	2.86	17.02	1.72	1.20	2.14
5	4	12629.7	1.80	3.29	45.45	23.07	2.88	0.60	5.51	1.96	0.34	0.56	0.67	7.18	2.59	0.25	0.41
6	5	33719.4	0.04	0.56	7.68	4.13	2.95	0.05	0.24	2.61	1.02	2.31	0.11	1.52	3.28	0.72	1.72
7	5	33904.9	2.74	2.47	30.14	20.74	3.19	0.09	0.00	2.43	2.19	6.17	0.93	6.42	2.95	0.29	0.94
8	5	30134.9	1.34	0.89	5.82	0.74	2.72	0.13	0.09	1.79	10.34	22.23	0.33	0.46	2.53	8.09	21.00
9	5	37276.5	3.34	2.17	42.54	18.86	2.37	0.13	0.05	1.71	5.54	9.72	0.47	4.50	2.35	3.28	4.81
10	5	30509.2	1.08	1.24	21.02	5.86	2.22	0.06	0.01	0.95	4.60	5.33	0.15	1.12	1.75	0.85	0.93
11	5	37666.3	2.00	1.52	25.56	9.33	3.32	0.06	0.00	2.32	4.42	5.04	0.19	2.16	3.00	1.01	1.35
12	5	36715.1	0.84	2.49	29.78	8.73	1.80	0.22	0.17	1.75	6.95	7.86	0.38	3.60	2.09	9.78	14.12
13	10	54719.9	5.39	3.75	75.00	51.41	3.32	0.03	0.04	3.67	1.98	3.66	0.84	17.39	4.45	0.55	1.02
14	2	7828.1	0.70	0.93	39.30	31.60	1.10	0.11	12.38	0.63	3.07	6.04	0.23	16.65	1.09	0.67	1.45
15	4	28799.9	3.95	2.01	56.38	24.84	2.75	0.08	0.03	4.42	5.43	12.20	0.36	7.88	3.90	1.19	2.41
16	3	37876.2	1.57	1.69	44.10	11.49	1.79	0.11	0.03	1.76	4.20	7.44	0.17	2.90	2.09	4.97	9.85
17	5	36202.9	0.00	1.71	8.22	4.33	2.37	0.25	0.24	2.16	5.26	6.82	0.32	2.00	2.79	3.84	4.97
18	5	32452.6	3.18	1.40	28.36	15.18	1.68	0.10	0.01	2.11	10.48	13.31	0.30	4.76	1.98	3.76	5.88
19	4	37367.3	1.90	2.09	46.75	17.61	2.33	0.11	0.10	1.72	13.58	18.80	0.36	4.18	2.38	6.52	10.79
20	5	40464.9	1.46	1.55	26.58	8.20	2.96	0.06	0.07	1.56	4.29	5.19	0.27	2.78	2.33	2.52	3.02
21	5	29052.6	5.06	2.72	49.22	30.78	2.16	0.12	0.09	1.45	2.17	2.66	0.63	9.06	2.26	0.51	0.73
22	4	15961.1	2.00	1.17	20.28	16.34	1.89	0.05	0.40	1.58	0.13	0.27	0.25	6.25	2.26	0.07	0.16
23	6	29438.2	5.17	2.32	41.02	28.40	2.91	0.07	0.00	1.54	3.93	6.03	0.56	9.47	2.37	0.36	0.54
24	2	3286.4	1.75	1.25	24.90	24.27	2.03	0.13	2.77	1.34	9.08	13.98	0.40	8.95	2.31	2.34	4.22
25	6	28704.0	0.00	0.87	3.43	2.33	2.91	0.14	0.17	4.14	7.59	8.51	0.27	0.75	3.72	8.86	10.23
26	4	12175.0	0.28	1.57	13.93	10.35	3.84	0.72	4.17	3.33	6.76	8.85	0.92	4.93	3.51	7.03	9.73
27	5	28067.9	3.10	4.23	52.22	44.34	2.72	0.31	7.46	2.19	0.48	0.74	1.43	24.40	2.56	0.42	0.67
28	5	19504.7	2.92	1.44	20.92	16.69	2.62	0.04	0.00	1.35	0.44	0.61	0.36	4.78	2.11	0.37	0.61
29	4	21752.3	1.98	1.34	15.18	11.87	2.40	0.04	0.00	2.13	0.56	0.70	0.30	4.05	2.61	0.51	0.71
30	4	17945.3	0.30	0.71	6.55	2.82	6.06	0.06	0.01	5.49	0.57	0.87	0.15	1.73	5.73	0.35	0.55
31	4	12093.4	0.38	1.28	28.80	23.23	2.64	0.05	1.24	2.51	2.78	2.98	0.42	14.55	3.16	0.82	0.87
32	5	37030.7	5.32	2.42	34.76	25.61	2.65	0.05	0.00	3.08	0.18	0.44	0.72	9.30	2.83	0.58	1.62
33	3	26560.4	0.97	1.64	26.23	20.48	2.65	0.33	1.80	1.92	1.13	0.97	0.68	12.07	2.00	0.53	0.53
34	5	24631.7	5.24	2.14	67.60	63.87	2.49	0.04	0.03	2.61	15.57	16.93	0.61	23.56	3.13	0.54	0.61
35	5	30863.5	0.66	1.51	15.72	6.08	2.46	0.04	0.02	2.34	17.25	20.99	0.21	2.42	2.96	3.79	5.91
36	5	31692.2	1.90	1.30	17.02	9.77	3.40	0.09	0.04	1.48	6.31	9.54	0.39	3.44	2.65	0.97	1.45
37	3	10944.2	4.87	1.27	29.13	22.04	1.91	0.04	0.01	1.32	0.46	0.63	0.38	10.17	1.73	0.57	0.74
38	6	30299.9	0.07	0.74	6.68	1.67	3.34	0.09	0.01	2.57	2.48	3.74	0.17	0.97	3.19	1.41	2.26
39	3	14162.5	0.63	1.01	9.83	7.73	1.86	0.07	3.82	1.18	0.55	1.19	0.17	3.47	1.64	0.69	1.30
40	2	4222.8	4.45	2.20	34.80	30.33	2.09	0.06	0.01	1.27	3.49	4.20	0.63	8.00	2.23	0.44	0.59
41	4	23585.9	2.65	0.89	20.08	15.09	4.79	0.19	3.08	4.35	0.20	0.42	0.35	9.05	3.94	0.68	1.34
42	4	22107.7	2.98	1.85	36.68	24.75	2.23	0.10	0.01	2.25	5.38	11.31	0.43	8.50	2.75	1.30	2.80
43	4	29336.8	1.98	1.64	14.93	11.04	2.83	0.15	0.10	1.19	2.77	4.43	0.57	5.25	2.01	0.50	0.84
44	3	13809.7	0.03	0.49	2.23	0.51	4.75	0.12	0.05	4.74	18.49	38.16	0.19	0.40	5.08	16.25	36.15
45	4	32284.9	2.40	1.18	28.73	23.85	2.17	0.31	2.27	1.56	4.19	5.92	0.46	7.63	2.44	3.10	4.34
46	5	27135.4	2.18	1.50	18.98	15.51	1.63	0.24	0.78	1.13	7.17	10.88	0.52	7.00	1.83	8.18	12.22
47	4	26544.9	1.55	1.51	14.43	9.96	3.70	0.69	1.31	3.49	4.44	6.49	0.89	3.45	3.55	5.66	6.81
48	4	23590.5	4.28	1.57	27.45	21.86	2.95	0.03	0.10	3.76	0.51	0.97	0.24	6.00	3.68	0.34	0.58
49	3	6197.0	3.80	1.80	25.13	20.32	3.72	0.08	0.00	3.03	5.72	8.87	0.57	7.43	3.84	0.93	1.37
50	3	6084.0	0.60	1.21	12.80	5.58	2.12	0.07	0.03	1.66	5.81	8.44	0.23	2.30	2.21	1.15	1.66
51	5	33771.6	0.00	0.58	8.04	4.89	2.15	0.06	0.03	1.32	2.53	3.22	0.18	4.30	2.20	0.96	1.67
52	3	15487.9	3.23	0.86	2.93	0.32	2.04	0.15	0.02	1.33	30.17	54.52	0.21	0.10	2.03	33.18	63.57
53	8	76846.7	0.40	1.17	13.46	6.96	2.77	0.02	0.01	2.92	5.41	7.21	0.24	3.01	3.60	1.87	1.67
54	4	31842.9	0.08	0.85	13.03	7.92	1.80	0.08	0.47	1.28	0.45	0.76	0.20	5.33	2.28	0.45	0.82
55	3	17051.6	3.83	5.08	110.93	97.34	1.99	1.77	41.77	1.98	0.56	0.97	2.77	61.03	2.44	0.64	1.11
56	3	49390.6	2.37	3.57	55.77	47.32	1.86	4.50	28.52	3.09	13.99	12.81	2.30	36.70	2.86	11.79	10.90
Mean:	4.6	27337.0	2.16	1.72	28.90	19.30	2.63	0.25	2.25	2.24	5.14	7.77	0.54	8.27	2.73	3.20	5.29

NOTE: HC, CO, NO_x all (gm/mi); SO_4 (mg/mi)
(1) Hot FTP CO with Bag III for Bag I
(2) SO_4 values adjusted to 0.030 wt. % fuel sulfur

Table 4

AVERAGE RESULTS BY MILEAGE INTERVALS

MILEAGE INTERVAL	# TESTS	IDLE CO(%)	FTP			50 mph CRUISE				CFDS			
			HC	CO	NOx	HC	CO	NOx	SO_4	HC	CO	NOx	SO_4
0-5	27	1.3	1.0	17.5	2.6	0.1	0.6	2.3	11.8	0.2	3.8	2.7	10.0
5-10	29	2.4	1.4	25.8	2.6	0.1	0.4	2.1	8.7	0.4	7.6	2.6	7.7
10-15	37	2.2	1.6	27.5	2.6	0.2	1.4	2.2	7.3	0.7	7.1	2.7	3.7
15-20	28	2.3	1.8	29.7	2.5	0.1	2.5	2.0	7.2	0.5	9.5	2.5	4.5
20-25	37	2.9	1.8	31.2	2.5	0.2	1.7	2.1	5.7	0.5	7.8	2.6	2.7
25-30	25	2.2	1.7	31.6	2.7	0.2	2.2	2.5	8.1	0.5	9.2	2.9	6.8
30-35	26	1.5	1.9	29.2	2.7	0.3	2.2	2.4	8.3	0.5	6.9	2.9	4.1
35-40	13	2.3	1.9	31.3	3.2	0.1	0.1	2.7	4.9	0.5	7.2	3.3	1.8
40-45	18	2.0	2.3	32.9	2.9	0.2	1.0	2.6	5.2	0.8	8.9	3.3	3.0
45-50	7	2.0	3.3	46.8	2.4	1.7	10.7	2.8	6.5	1.3	19.1	3.0	6.7
>50	9	2.5	2.4	38.0	2.9	0.1	0.1	2.7	4.5	0.5	7.2	3.2	2.4

NOTE: MILEAGE INTERVALS IN THOUSANDS OF MILES

HC, CO, NO_x, ALL (gm/mi)

SO_4 MEASUREMENTS NORMALIZED TO 0.030 WT.% FUEL SULFUR, IN (mg/mi)

EMISSION TRENDS WITH MILEAGE ACCUMULATION: INDIVIDUAL VEHICLES

Least-squares-regressions of emissions results for tests on individual vehicles have been used to compute mileage accumulation trends. The computational procedure is similar to that used to determine "deterioration factors" as defined in federal certification procedures (10). In new car certification, the change of an emissions parameter with accumulated mileage is computed as the ratio of the emissions at 50,000 miles to emissions at 4,000 miles, as determined by the straight line regression of test data. This definition of deterioration could not be applied here since all cars did not accumulate the same number of miles, and the emission data sets frequently exhibited sufficient scatter so as to preclude extrapolation to a common 50,000 mile basis as required by the "deterioration factor" definition.

A common 10,000 mile basis for comparison of emissions trends among test group cars was adopted to avoid extrapolation difficulties. For each vehicle, a straight line regression was used to compute a change in emissions for this common 10,000 mile basis. Dividing this emission change per 10,000 miles by the mean of the emission data set used for the regression yields a normalized "percent change in 10,000 miles". These values are not a comparison of the absolute emission rates among the test group vehicles, and only indicate how an individual vehicle's emissions changed as a percentage of its own average. The "percent change in 10,000 miles" values for the 56 test group cars thus serve as a basis for additional comparisons; histograms of these values for the test group give a picture of the variability in trends with accumulated miles for various emission parameters and test cycles.

Hydrocarbon Trends

Figure 2 contains histograms of the mileage accumulation trends in HC emissions for the test group for FTP, CFDS and 50 mph cruise. The "percent change in 10,000 mile" abscissa ranges from -100% to +100%, the ordinate, "test group cars", is expressed as a percentage of the vehicle sample. In a few instances the least squares regression lines resulted in trends in excess of $\pm$ 100% change in 10,000 miles, and these have been arbitrarily excluded in the preparation of histograms (the number of vehicles used being noted on each histogram). The mean HC trend for the FTP is a 14% increase in emissions per 10,000 miles. CFDS and 50 mph cruise are similar to the FTP, although the absolute emissions levels in these test modes are lower (Table 4).

Carbon Monoxide Trends

Figure 3 shows mileage accumulation trend results for CO emissions in the same format as Figure 2. Idle CO trends are also presented in this figure. For each test mode in Figure 3 the mean change is only a few percent, consistent with the relatively unchanged emissions in the 5,000 mile intervals of Table 4.

The range of "percent change in 10,000 miles" of FTP CO appears to be less than either the CFDS or 50 mph cruise. This must be viewed in light of

Fig. 2 MILEAGE ACCUMULATION TRENDS FOR HC EMISSIONS

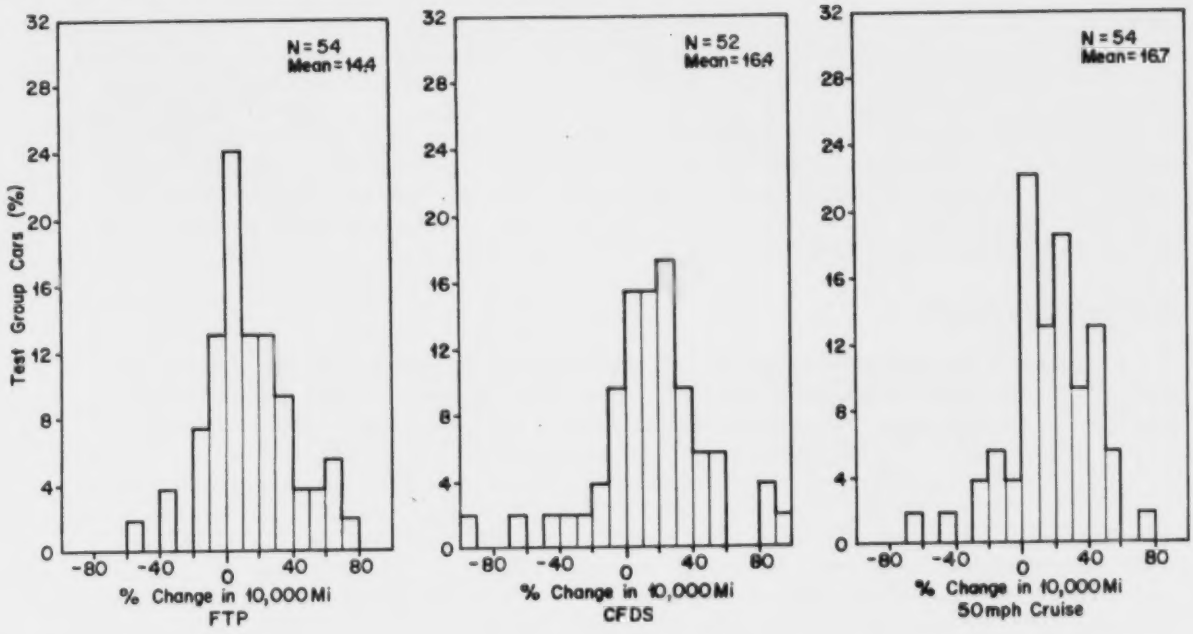
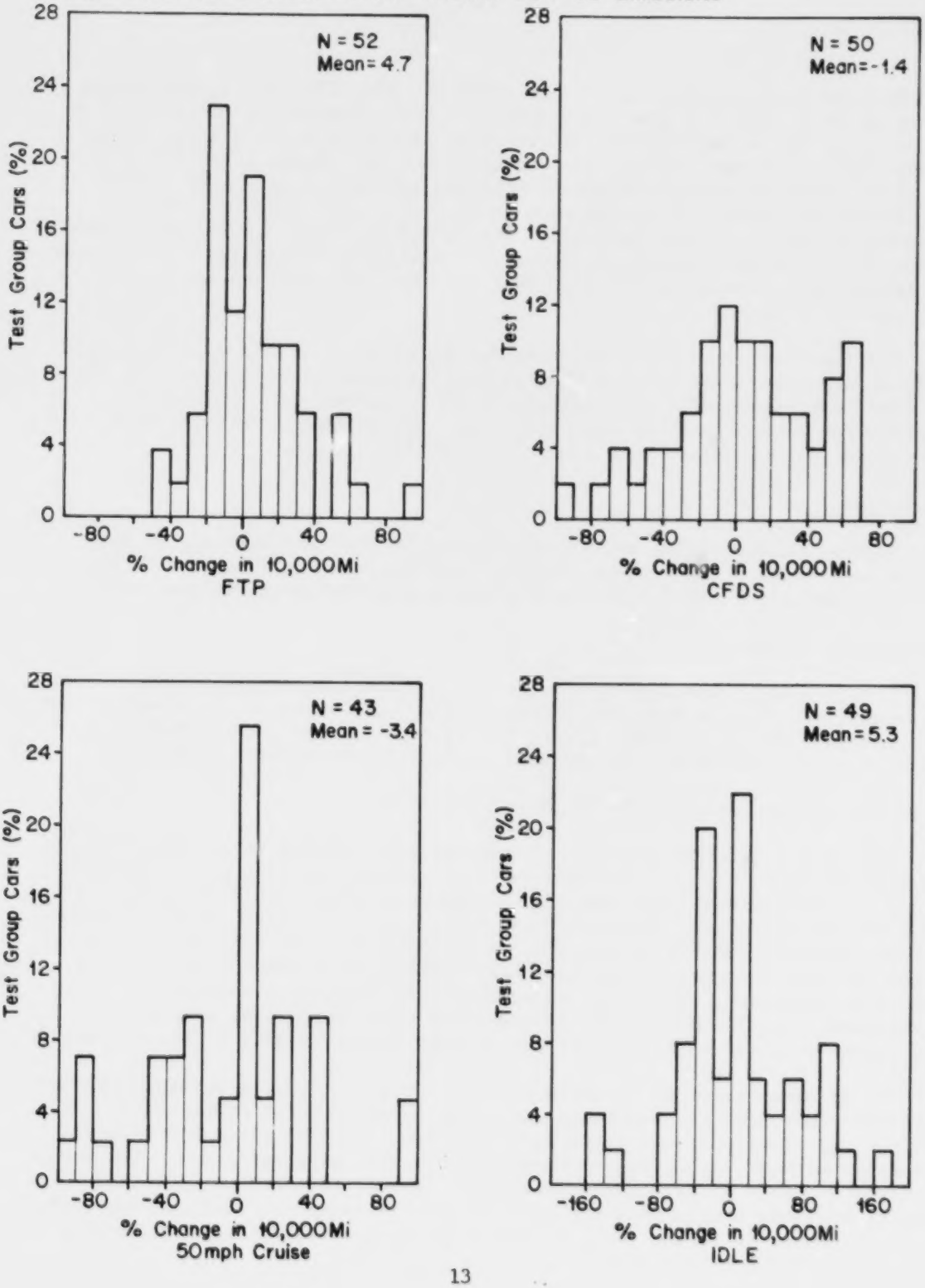


Fig. 3 MILEAGE ACCUMULATION TRENDS FOR CO EMISSIONS



the absolute CO mass emissions in each segment, FTP, CFDS and 50 mph cruise averaging 29.1, 7.8, 1.6 g/mi respectively. Small changes in emissions from test to test for an individual vehicle often have a greater relative effect on the CFDS and 50 mph cruise. In Figure 4 "percent change in 10,000 miles" values for idle CO and FTP CO are plotted against each other. Car number identifiers are indicated beside each point. The results of test data presented graphically in Figure 4 are summarized in Table 5. Trends in idle CO and FTP CO values correspond except for values for 6 vehicles with increasing idle CO and decreasing FTP CO. Four of these six vehicles are Fords (air pump vehicles).

Two institutional fleets began to use HC/CO analyzers to maintain their vehicles near the conclusion of this study. This change was unknown to us at the time, but corresponds to observations of decreasing idle CO values observed for several high mileage vehicles. Ten of the 21 vehicles with decreasing idle CO values were from these two fleets.

NO_x Trends

Figure 5 shows histograms of NO_x trends for the FTP, CFDS and 50 mph cruise test modes. The range of mileage accumulation trend values for NO_x are less than for HC and CO, and are also more consistent among test modes.

Particulate Sulfate

Figure 6 shows the effect of mileage accumulation on particulate sulfate emission rates for the CFDS and 50 mph cruise, with emission rates normalized to a common 0.030 wt % sulfur fuel. The substantial percentage changes are again in part a reflection of sensitivity due to low emission rates.

EMISSIONS RESULTS CATEGORIZED BY INDIVIDUAL TESTS

Above, the data for each test group car were treated as an independent, mileage-related data set. Analysis of test results for mileage accumulation trends from individual cars implicitly assumes a relationship among the test data for any given car. The fact that tests were all performed on the same vehicle does not totally define this relationship for the test data since events between test points (particularly vehicle maintenance) can abruptly influence emissions. The range of positive and negative trends in the above histograms, especially idle CO, demonstrates this point. The predominant such event observed in this study was a major change in idle CO between tests.

As an alternative to treating the data on each car as a mileage dependent data set, each test was considered as being independent of other tests. In Table 6 the results of all tests have been tabulated for various subclassifications without regard to the cars on which they were performed. The number of tests and cars in each classification is indicated. Tables 7, 8, and 9 are similar to Table 6 with only the cars of the indicated manufacturer included. Sulfate results in Tables 6, 7, 8, and 9 are as measured, and not normalized to 0.030 wt % for sulfur fuel.

Fig. 4 Comparison of Idle CO and FTP CO Trends

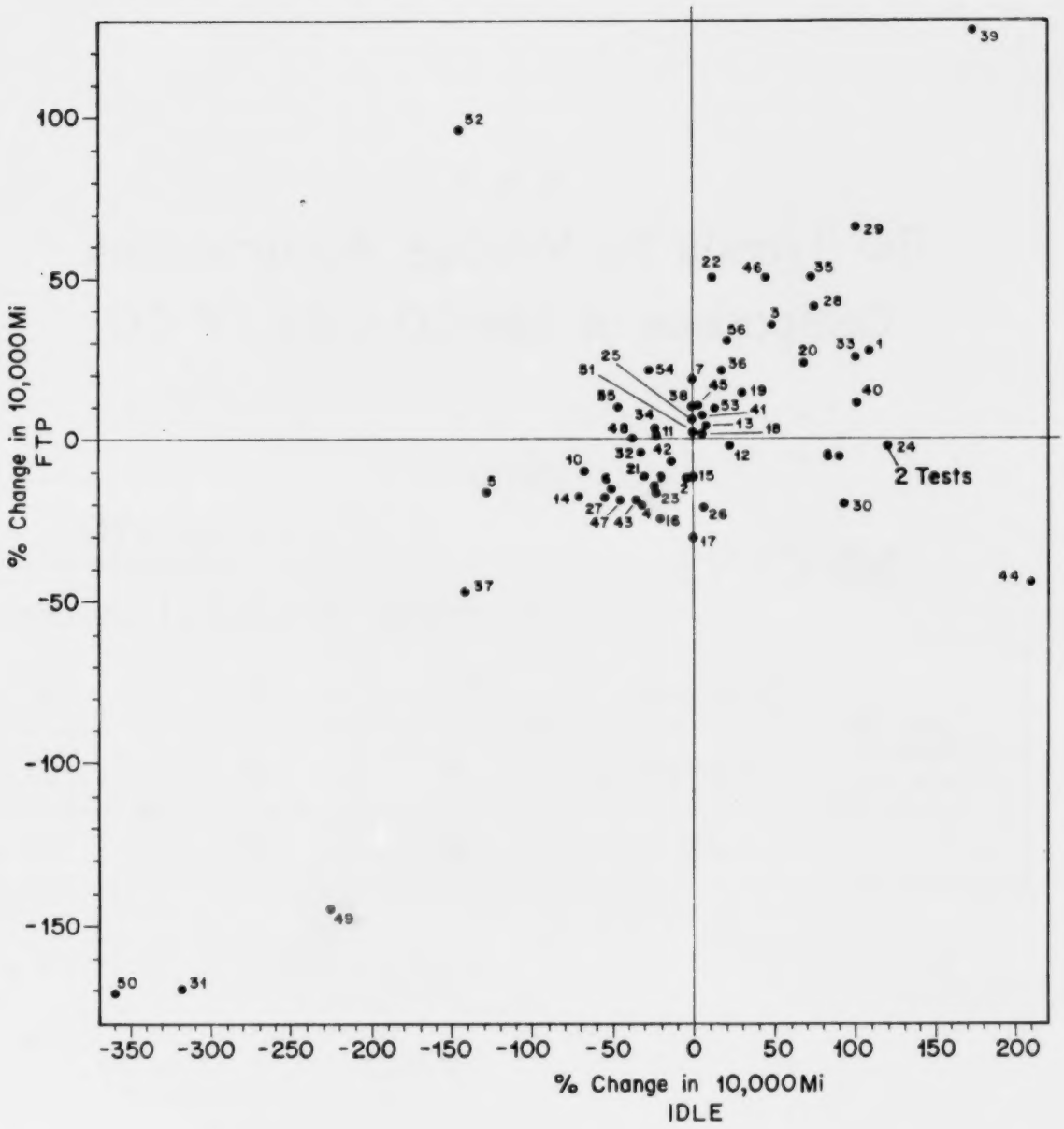


Table 5

CO Trends by Mileage Accumulation
Comparison of Idle CO and FTP CO

56 CARS		FTP CO (gm/mi)		
		increasing ↑	decreasing ↓	unchanged –
IDLE CO(%)	increasing ↑	19	6	2
	decreasing ↓	4	19	0
	unchanged –	4	2	0

Fig. 5 MILEAGE ACCUMULATION TRENDS FOR NO_x EMISSIONS

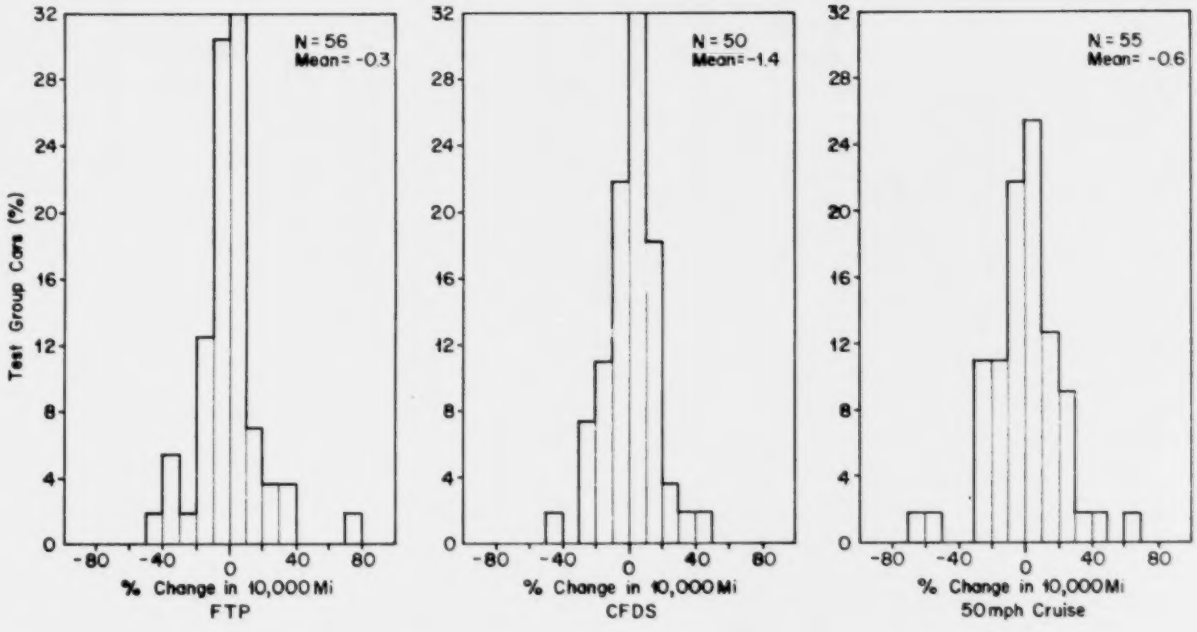


Fig. 6 MILEAGE ACCUMULATION TRENDS FOR SULFATE EMISSIONS

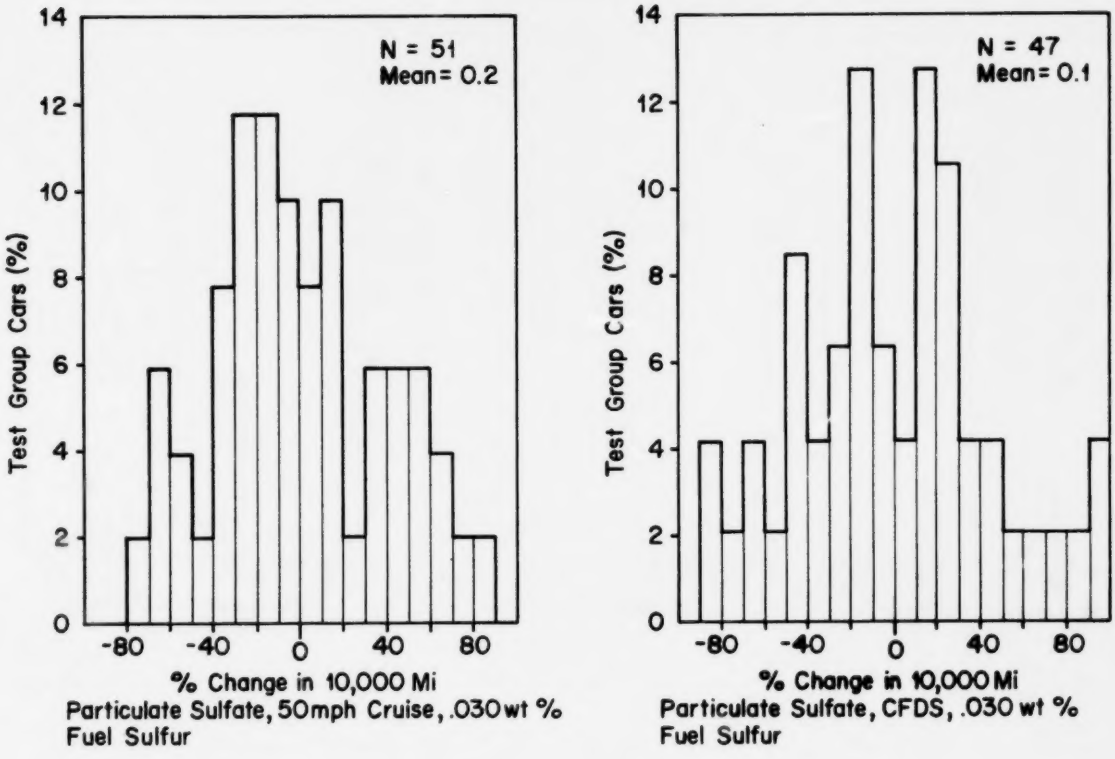


TABLE 6

Average Emission Results
All Tests, All Manufacturers

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP gm/mi HC	FTP gm/mi CO	FTP gm/mi NO_x	1 Hr 50 mph Cruise gm/mi HC	1 Hr 50 mph Cruise gm/mi CO	1 Hr 50 mph Cruise gm/mi NO_x	1 Hr 50 mph Cruise mg/mi SO_4	CFDS gm/mi HC	CFDS gm/mi CO	CFDS gm/mi NO_x	CFDS mg/mi SO_4
All	256	56	2.2	1.7	29.1	2.7	0.2	1.6	2.3	5.0	0.5	7.8	2.8	3.1
FTP CO < 15 gm/mi	93	31	0.4	0.9	8.0	2.8	0.1	0.2	2.4	7.3	0.2	1.8	3.0	6.0
FTP CO < 15 gm/mi, HC < 1.5 gm/mi	87	28	0.4	0.8	7.8	2.8	0.1	0.1	2.4	7.9	0.2	1.7	2.9	6.1
FTP CO < 15 gm/mi, HC < 1.5 gm/mi NO_x < 3.1 gm/mi	66	26	0.5	0.8	8.0	2.3	0.1	0.1	1.9	7.8	0.2	1.9	2.5	6.4
Idle CO ≤ 1%	116	39	0.2	1.0	12.9	2.7	0.1	0.6	2.3	6.9	0.2	2.4	2.9	5.5
Idle CO > 1%	140	47	3.8	2.3	42.5	2.6	0.3	2.5	2.2	3.5	0.8	12.3	2.7	1.2
FTP CO > 45 gm/mi	51	18	4.9	3.4	70.3	2.6	0.5	5.0	2.7	4.7	1.2	21.4	3.1	0.7
Stall in Bag I of FTP	58	31	1.8	1.5	24.6	2.4	0.1	0.9	2.1	7.8	0.4	6.5	2.6	5.2
Fleet Vehicles	143	29	2.4	1.9	35.1	2.5	0.2	1.3	2.2	5.1	0.5	8.3	2.7	2.3
Private Vehicles	102	26	2.1	1.6	22.6	2.9	0.2	2.3	2.5	4.5	0.5	7.9	3.0	3.5
0 - 15,000 miles	93	45	2.0	1.4	24.1	2.6	0.2	0.9	2.2	6.1	0.5	6.3	2.7	4.0
15,000 - 30,000 miles	90	51	2.5	1.8	30.9	2.6	0.2	2.1	2.2	4.5	0.5	8.7	2.6	2.7
30,000 - 45,000 miles	57	37	1.9	2.0	30.8	2.9	0.2	1.4	2.6	4.3	0.6	7.6	3.1	2.3
45,000 miles	16	13	2.3	2.8	41.9	2.7	0.8	4.7	2.6	4.5	0.9	12.4	3.1	3.0

TABLE 7

Average Emission Results
General Motors Vehicle Tests

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP gm/mi			1 Hr 50 mph Cruise gm/mi			mg/mi	CFDS gm/mi			mg/mi
				HC	CO	NO_x	HC	CO	NO_x	SO_4	HC	CO	NO_x	SO_4
All General Motors Vehicles	95	21	1.6	1.4	21.8	2.7	0.1	2.4	2.2	2.3	0.4	8.1	2.7	1.8
FTP CO < 15 gm/mi	46	13	0.2	0.8	8.2	2.8	0.1	0.1	2.2	3.3	0.2	2.3	2.8	2.8
FTP CO < 15 gm/mi, HC < 1.5 gm/mi	45	13	0.2	0.7	8.1	2.8	0.0	0.1	2.2	3.3	0.1	2.3	2.8	2.9
FTP CO < 15 gm/mi, HC < 1.5 gm/mi, NO_x < 3.1 gm/mi	36	12	0.2	0.7	8.4	2.3	0.0	0.1	1.7	3.8	0.1	2.5	2.4	3.4
Idle CO ≤ 1%	53	15	0.1	0.9	9.9	2.7	0.1	0.3	2.2	3.8	0.2	2.8	2.8	3.0
Idle CO > 1%	42	14	3.6	2.1	36.8	2.7	0.2	5.1	2.3	0.5	0.7	14.8	2.6	0.4
FTP CO > 45 gm/mi	7	3	3.8	4.3	84.3	2.6	0.9	20.7	2.3	0.4	1.9	44.5	2.6	0.4
CFDS SO_4 > 10 mg/mi	6	2	0.0	0.7	9.2	1.9	0	0	1.4	13.4	0.1	1.0	2.1	14.9
Fleet Vehicles	29	6	0.7	1.1	14.5	2.4	0.1	1.3	1.9	1.6	0.3	5.8	2.7	1.1
Private Vehicles	55	14	2.4	1.8	27.8	3.0	0.2	3.5	2.6	1.2	0.6	10.7	2.9	0.7
0 - 15,000 miles	33	16	1.6	1.1	18.8	2.4	0.1	1.5	1.9	2.4	0.3	6.5	2.4	1.8
15,000 - 30,000 miles	40	19	2.1	1.7	26.0	2.7	0.2	3.6	2.3	1.8	0.5	10.2	2.8	1.6
30,000 - 45,000 miles	19	11	0.9	1.2	17.7	3.2	0.1	1.2	2.8	2.9	0.4	6.0	3.2	2.1
45,000 miles	3	3	1.3	2.7	25.8	2.2	0.2	4.0	2.4	5.8	0.8	9.9	2.7	4.4

TABLE 8

Average Emission Results
Ford Vehicle Tests

Classification of Tests	No. Tests	No. Cars	Idle CO%	FTP gm/mi HC	FTP gm/mi CO	FTP gm/mi NO_x	1 Hr 50 mph Cruise gm/mi HC	1 Hr 50 mph Cruise gm/mi CO	1 Hr 50 mph Cruise gm/mi NO_x	1 Hr 50 mph Cruise mg/mi SO_4	CFDS gm/mi HC	CFDS gm/mi CO	CFDS gm/mi NO_x	CFDS mg/mi SO_4
All Ford Vehicles	38	10	1.3	1.1	13.6	2.8	0.3	1.8	2.5	9.6	0.5	4.2	2.9	9.3
FTP CO < 15 gm/mi	24	7	0.8	0.9	5.4	3.1	0.3	0.5	3.0	13.0	0.4	1.1	3.3	13.5
FTP CO < 15 gm/mi, HC < 1.5 gm/mi	21	7	0.9	0.8	4.5	3.1	0.2	0.2	3.0	13.8	0.3	0.8	3.3	14.2
FTP CO < 15 gm/mi, HC < 1.5 gm/mi, NO_x < 3.1 gm/mi	12	5	1.4	0.8	3.4	2.2	0.2	0.1	2.1	16.1	0.3	0.5	2.5	16.5
Idle CO ≤ 1%	23	8	0.2	0.9	8.7	3.1	0.3	1.9	3.0	12.2	0.4	2.7	3.2	12.8
Idle CO > 1%	15	6	3.0	1.4	21.1	2.3	0.3	1.5	1.8	5.7	0.6	6.4	2.4	3.9
FTP CO > 45 gm/mi	0	0	-	-	-	-	-	-	-	-	-	-	-	-
CFDS SO_4 > 10 mg/mi	12	6	0.8	0.8	3.9	3.2	0.2	0.3	2.9	18.0	0.3	0.6	3.4	20.8
Fleet Vehicles	7	2	1.2	0.9	15.4	2.3	0.1	3.6	1.5	8.3	0.3	5.1	2.1	6.0
Private Vehicles	31	8	1.3	1.2	13.2	2.9	0.3	1.3	2.7	9.9	0.5	4.0	3.1	10.0
0 - 15,000 miles	18	8	0.9	1.0	8.3	3.4	0.3	1.3	3.0	11.2	0.4	2.2	3.5	11.5
15,000 - 30,000 miles	15	9	1.8	1.2	18.7	2.2	0.2	1.9	2.1	8.9	0.4	6.2	2.5	7.7
30,000 - 45,000 miles	5	5	1.2	1.4	17.6	2.1	0.3	3.1	2.0	6.0	0.6	5.4	2.3	5.8
45,000 miles	0	0												

TABLE 9

Average Emission Results
Chrysler Vehicle Tests

Classification of Tests	No. Tests	No Cars	Idle CO%	FTP gm/mi			1 Hr 50 mph Cruise gm/mi				CFDS gm/mi			
				HC	CO	NO_x	HC	CO	NO_x	mg/mi SO_4	HC	CO	NO_x	mg/mi SO_4
All Chrysler Vehicles	120	24	2.9	2.2	39.8	2.6	0.2	1.0	2.3	5.8	0.6	8.7	2.8	2.2
FTP CO < 15 gm/mi	22	10	0.6	1.0	10.5	2.5	0.1	0.0	2.3	9.8	0.2	1.4	2.8	4.7
FTP CO < 15 gm/mi, HC < 1.5 gm/mi,	20	8	0.6	0.9	10.5	2.4	0.1	0.0	2.2	10.3	0.2	1.3	2.7	5.1
FTP CO < 15 gm/mi, HC < 1.5 gm/mi, NO_x < 3.1 gm/mi	17	8	0.6	0.9	10.2	2.2	0.1	0.0	2.1	11.1	0.2	1.3	2.5	5.9
Idle CO ≤ 1%	38	15	0.3	1.2	19.3	2.6	0.1	0.0	2.2	8.3	0.2	1.3	2.8	4.8
Idle CO > 1%	82	24	4.1	2.6	49.3	2.6	0.3	1.4	2.3	4.6	0.8	12.1	2.8	1.0
FTP CO > 45 gm/mi	44	14	5.1	3.2	68.1	2.6	0.5	2.5	2.7	5.3	1.1	17.7	3.2	0.8
CFDS SO_4 > 10 mg/mi	19	11	1.9	1.4	30.3	2.4	0.1	0.0	2.4	18.5	0.3	5.9	2.7	6.9
Fleet Vehicles	104	20	3.0	2.3	42.2	2.5	0.3	1.1	2.3	5.9	0.6	9.1	2.8	2.4
Private Vehicles	16	4	2.5	1.6	22.9	3.0	0.1	0.0	1.9	5.1	0.5	5.9	2.7	0.9
Police Cruisers	28	4	3.2	2.6	50.8	2.8	0.5	3.1	3.2	4.6	0.8	14.9	3.7	2.3
Fleet -- No Police Cars	76	16	2.9	2.1	39.3	2.4	0.2	0.4	2.0	6.4	0.6	7.0	2.5	2.4
Fleet and Private Vehicles -- No Police Cars	92	20	2.8	2.0	36.4	2.5	0.3	0.2	2.0	6.2	0.6	6.8	2.5	2.2
0 - 15,000 miles	40	20	2.9	1.7	35.9	2.4	0.1	0.1	2.1	7.0	0.6	7.7	2.5	2.7
15,000 - 30,000 miles	34	22	3.4	2.1	41.5	2.6	0.1	0.3	2.1	5.9	0.5	8.0	2.6	1.8
30,000 - 45,000 miles	33	22	2.5	2.6	40.4	2.8	0.2	1.2	2.5	4.9	1.0	8.9	3.2	1.9
45,000 miles	13	10	2.5	2.8	45.5	2.8	1.0	4.9	2.7	4.2	0.9	13.0	3.2	2.6

Tables 6, 7, 8, and 9 were used to evaluate the cars and tests against various emission criteria. Applicable emission standards for these vehicles are 1.5/15/3.1 (gm/mi) for HC/CO/NO_x respectively. Table 10 is extracted from Tables 6-9 and indicates the number of cars and tests meeting various combinations of these emission standards. The idle CO $\leq$ 1% criteria shows a general correspondence to the FTP CO $\leq$ 15 gm/mi criteria.

Table 10

TESTS GROUPED BY EMISSION CUT POINTS

	Tests / Cars	ALL TESTS	GM	FORD	Chrysler
ALL TESTS	Tests	253	95	38	120
	Cars	55	21	10	24
FTP: CO $\leq$ 15	Tests	92	46	24	22
	Cars	30	13	7	10
FTP: CO $\leq$ 15, HC $\leq$ 1.5	Tests	86	45	21	20
	Cars	28	13	7	8
FTP: CO $\leq$ 15, HC $\leq$ 1.5, $NO_x \leq$ 3.1	Tests	65	36	12	17
	Cars	25	12	5	8
IDLE CO $\leq$ 1%	Tests	114	53	23	38
	Cars	38	15	8	15
IDLE CO > 1%	Tests	139	42	15	82
	Cars	44	14	6	24
CFDS SO_4 > 10 mg/mi	Tests	37	6	12	19
	Cars	19	2	6	11

NOTE: 3 tests on 1 AMC vehicle not included
HC, CO, NO_x all (gm/mi)

SECTION 4

FUEL ECONOMY

LABORATORY AND OVER-THE-ROAD DATA

Laboratory fuel economy was measured by the carbon balance technique for FTP, CFDS and 50 mph cruise segments of each vehicle test. HFET fuel economy was added in the final few months of testing. Average over-the-road (OTR) fuel economy and vehicle speed were obtained between vehicle test points by use of fuel and hour meters installed on each car at the beginning of the project. Further experimental details are presented in Section 8 of this report.

Table 11 lists the average fuel economy results obtained for each of the test group cars throughout the two years of testing. The HFET was included as a part of the test sequence at test #218 in August 1977; by that time 12 vehicles had left the project. Except for three vehicles with more than one test after this date, HFET and Combined fuel economy reported are for the final test on each vehicle. Table 11 also gives EPA fuel economy results for certification vehicles corresponding to test group vehicles by engine family and inertia weight specification(20-22). Figure 7 shows speed versus time traces for the three EPA driving schedules used in this study; Table 12 gives some characteristics of the various laboratory test cycles.

TABLE 12. TEST MODE CHARACTERISTICS

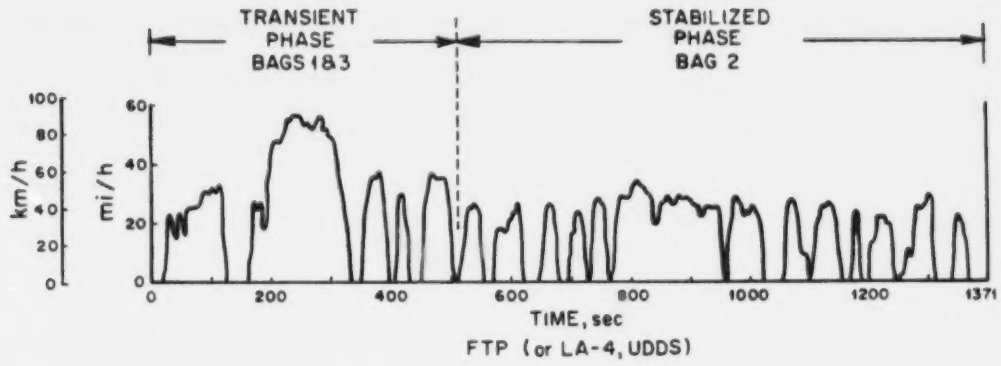
	length (miles)	average speed (mph)	max speed (mph)	time (sec.)	stops/mile	time at idle (%)
FTP	11.1	21.3	56.7	1877	2.1	19.2
HFET	10.2	48.2	59.9	765	0.1	1.0
Combined	10.7	28.4	59.9	1135	0.2	2.1
CFDS	13.5	34.8	57.0	1398	0.2	2.3
50 Cruise	50.0	50.0	50.0	3600	0.0	0.0

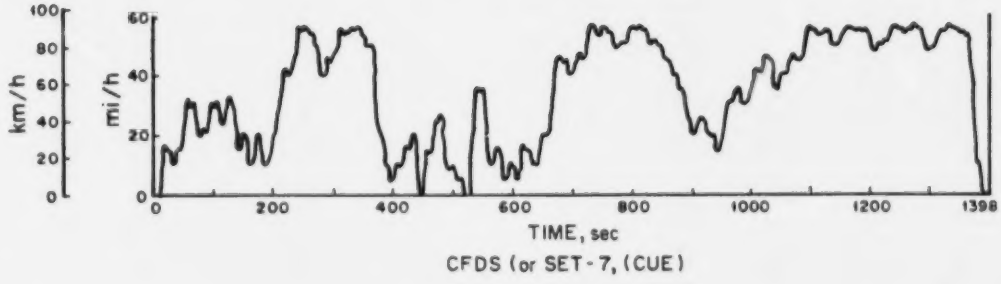
Average fuel economy from carbon balance and OTR measurements are shown graphically in Figure 8 as a function of average vehicle speed for the various test segments. The OTR data covers 1.5 million vehicle miles and averaged 32.8 mph and 15.1 mpg.

TABLE 11

AVERAGE FUEL ECONOMY FROM TEST GROUP VEHICLES

	AEL Carbon Balance MPG Measurements					AEL Over The Road Measurements		EPA MPG		
Car #	FTP	HFET	Combined	CFDS	50 Cruise	Avg MPH	Avg MPG	FTP	HFET	Combined
1	9.9	15.5	12.1	13.3	15.4	30.5	10.6	10	14	11
2	12.1	--	--	15.8	17.9	30.5	11.7	14	18	15
3	9.1	--	--	13.0	14.9	27.6	7.1	10	15	12
4	10.3	17.6	13.4	14.0	18.4	33.0	11.9	12	17	14
5	16.9	25.9	20.9	23.0	25.4	26.8	14.3	17	23	19
6	11.9	--	--	16.0	18.0	35.1	13.2	14	18	15
7	16.6	28.1	22.3	22.4	25.9	33.6	14.9	17	23	19
8	13.6	18.0	17.2	16.8	18.3	34.2	11.6	14	18	16
9	11.3	22.2	13.8	16.7	18.8	38.4	13.1	12	17	14
10	16.9	25.1	21.0	22.8	26.3	50.6	21.7	17	23	19
11	16.9	23.8	19.0	23.2	26.3	34.2	18.2	17	23	19
12	10.2	13.4	11.3	13.3	17.1	39.2	11.3	12	17	14
13	9.4	--	--	13.6	15.6	37.0	8.2	10	15	12
14	8.5	--	--	11.7	13.0	37.6	8.3	10	14	11
15	10.6	17.8	13.6	14.6	18.6	28.2	13.5	12	17	14
16	10.7	17.6	13.4	14.6	18.6	33.6	12.4	12	17	14
17	11.2	--	--	15.2	17.5	31.6	11.0	14	18	15
18	10.9	16.7	13.2	14.4	18.3	37.3	13.2	12	17	14
19	11.0	15.8	12.4	14.7	17.7	38.7	13.7	12	17	14
20	16.7	25.2	19.4	22.8	26.3	38.6	17.8	16	23	20
21	16.1	23.1	18.3	22.2	26.1	37.3	16.4	18	23	20
22	15.3	--	--	20.5	24.1	29.0	15.2	17	25	20
23	16.0	22.8	18.3	21.6	25.6	38.2	18.4	17	23	19
24	9.5	--	--	13.2	14.9	37.1	12.4	10	14	11
25	19.3	29.2	22.7	25.8	31.7	34.1	23.8	24	34	27
26	11.6	17.4	13.9	15.3	18.1	27.5	12.2	13	19	15
27	14.2	23.4	19.9	19.7	23.9	28.5	14.1	15	23	18
28	16.7	23.6	19.4	21.9	24.7	21.8	14.9	18	23	20
29	17.9	33.5	23.3	26.3	34.1	40.3	25.8	22	35	26
30	16.1	--	--	21.1	24.3	34.1	24.5	15	19	17
31	12.0	15.9	13.4	15.6	17.6	19.2	9.7	13	18	15
32	20.2	35.0	26.3	28.1	34.3	35.2	23.7	19	28	22
33	15.0	21.5	17.5	18.5	21.6	40.2	19.2	17	23	19
34	9.8	16.9	12.5	13.8	17.7	36.8	12.8	13	17	14
35	10.1	16.6	12.6	14.1	17.9	36.9	12.5	13	17	14
36	18.0	23.6	20.3	22.7	25.4	36.4	17.4	18	23	20
37	15.9	--	--	20.4	23.1	26.6	16.7	16	21	18
38	15.5	21.3	17.5	19.9	22.8	34.1	17.6	16	23	19
39	11.5	--	--	15.7	17.7	34.2	13.4	15	21	17
40	12.4	--	--	16.6	19.3	23.9	10.7	13	18	15
41	19.8	27.9	22.3	26.6	30.0	35.2	20.3	19	28	22
42	11.9	19.7	14.7	16.5	20.8	26.8	13.1	13	17	15
43	17.6	25.6	20.9	22.9	25.9	31.1	21.8	18	23	20
44	16.9	20.5	17.7	19.9	21.6	22.8	15.7	16	21	18
45	10.7	16.5	13.1	14.7	17.3	33.0	15.6	11	16	13
46	18.0	27.0	21.2	24.3	28.1	32.5	20.4	22	31	26
47	12.1	19.7	15.2	16.6	19.9	35.7	16.4	13	19	15
48	23.6	34.3	27.6	31.7	36.9	25.7	22.8	30	39	33
49	17.3	25.0	20.9	22.4	25.9	19.8	--	18	23	20
50	10.2	14.2	11.6	13.7	15.5	24.1	--	12	16	13
51	12.4	17.3	14.2	16.3	19.0	31.9	13.5	14	19	16
52	14.6	19.5	16.5	17.8	20.3	27.6	14.4	16	21	18
53	9.7	17.8	13.9	13.6	16.2	36.3	8.7	11	15	13
54	13.3	18.1	15.3	16.8	19.9	32.2	13.1	14	19	16
55	11.6	17.3	13.9	15.2	17.7	28.8	12.0	13	18	14
56	8.1	13.2	10.0	11.4	13.8	45.4	--	9	17	11
Means:	13.7	21.4	17.0	18.3	21.5	32.8	15.1	15.0	20.6	17.0
STD. DEV.	3.5	5.5	4.2	4.6	5.4	6.0	4.4	3.9	5.2	4.3





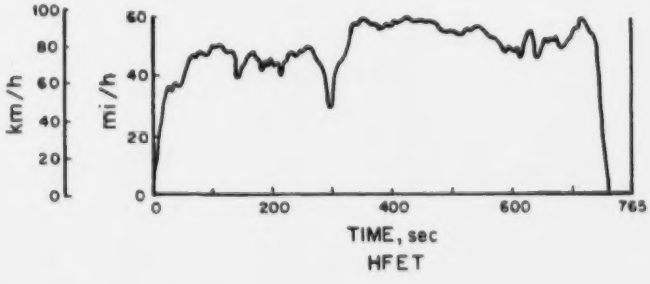


Figure 7

FTP, CFDS AND HFET DRIVING SCHEDULE (SPEED vs TIME)

Vehicle test group averages are presented for measured carbon balance FTP, HFET, CFDS and 50 mph cruise fuel economy at the bottom of Table 11. The EPA certification FTP fuel economy value of 15.0 mpg was in very close agreement to the measured OTR value of 15.1 mpg. Measured FTP fuel economy averaged 9% less than the OTR economy while the HFET and 50 mph cruise values overestimated the actual OTR economy by 41 and 42% respectively. Figures 9, 10 and 11 show the same results as Figure 7 for three engine family groups: Chrysler 225 CID I-6 cylinder, Chrysler 318 CID V-8, and Buick 350 CID V-8, respectively. Laboratory fuel economy results within these engine family groupings are quite uniform as seen by the $\pm$ 1σ bounds indicated.

Fuel Economy Trends With Mileage Accumulation

Plots of fuel economy vs. mileage accumulation were prepared for each test group vehicle. From these, data trends of fuel economy with increasing vehicle age can be evaluated. Figures 12, 13 and 14 are typical of the variety of fuel economy results obtained on three test group vehicles.

For most vehicles the fuel economy is relatively unchanged with mileage. Some long-term drift, both increasing and decreasing fuel economy, is observed as in Figures 12 and 13. Large jumps in fuel economy between two test points, such as in Figure 14, are not uncommon however. It has proved impossible to systematically determine the reasons for such changes in every case. Change in vehicle driver, rapid deterioration of drive-train, major and minor maintenance, etc., are not part of the data base, making correlation of fuel economy with all pertinent vehicle parameters impossible. Increases in fuel economy have been noted for several (but not all) vehicles when idle CO level dropped significantly.

Fuel economy and mileage accumulation data were fitted with straight lines from which slopes, normalized to a 10,000 mile basis, were computed in the same manner as for emissions trend analysis as in Section 3. The slopes from all vehicles were then used to prepare histograms showing percentage change in fuel economy per 10,000 miles for the test group. Figure 15 contains the histograms for the FTP, CFDS and 50 mph cruise. In all three cases, an increase of approximately 2% fuel economy per 10,000 miles was found.

Analysis of OTR Fuel Economy Results

The average fuel economy and vehicle speed data between laboratory test points has been analyzed for seasonal variation and effect of vehicle inertia weight. Fuel economy from all intervals was first averaged for each car, and the ratio of fuel economy in each interval to the overall average for that vehicle computed. Data from all cars and all intervals were then plotted against the month in the year, computed as the midpoint between test dates. Figure 16 shows these fuel economy results, and Figure 17 shows average vehicle speed plotted in the same manner. From these figures, no seasonal shifts in vehicle economy or speed are apparent. Seasonal changes may be obscured by the method of using the calendar midpoint to represent the interval between tests. The range of fuel economy and speed variations shown in Figures 16 and 17 give an indication of the OTR variability for these parameters. Average vehicle

Figure 8

FUEL ECONOMY BY TEST MODE

mpg vs. mph

56 Vehicles, 256 Emissions Tests,
1,530,873.7 Over The Road Miles

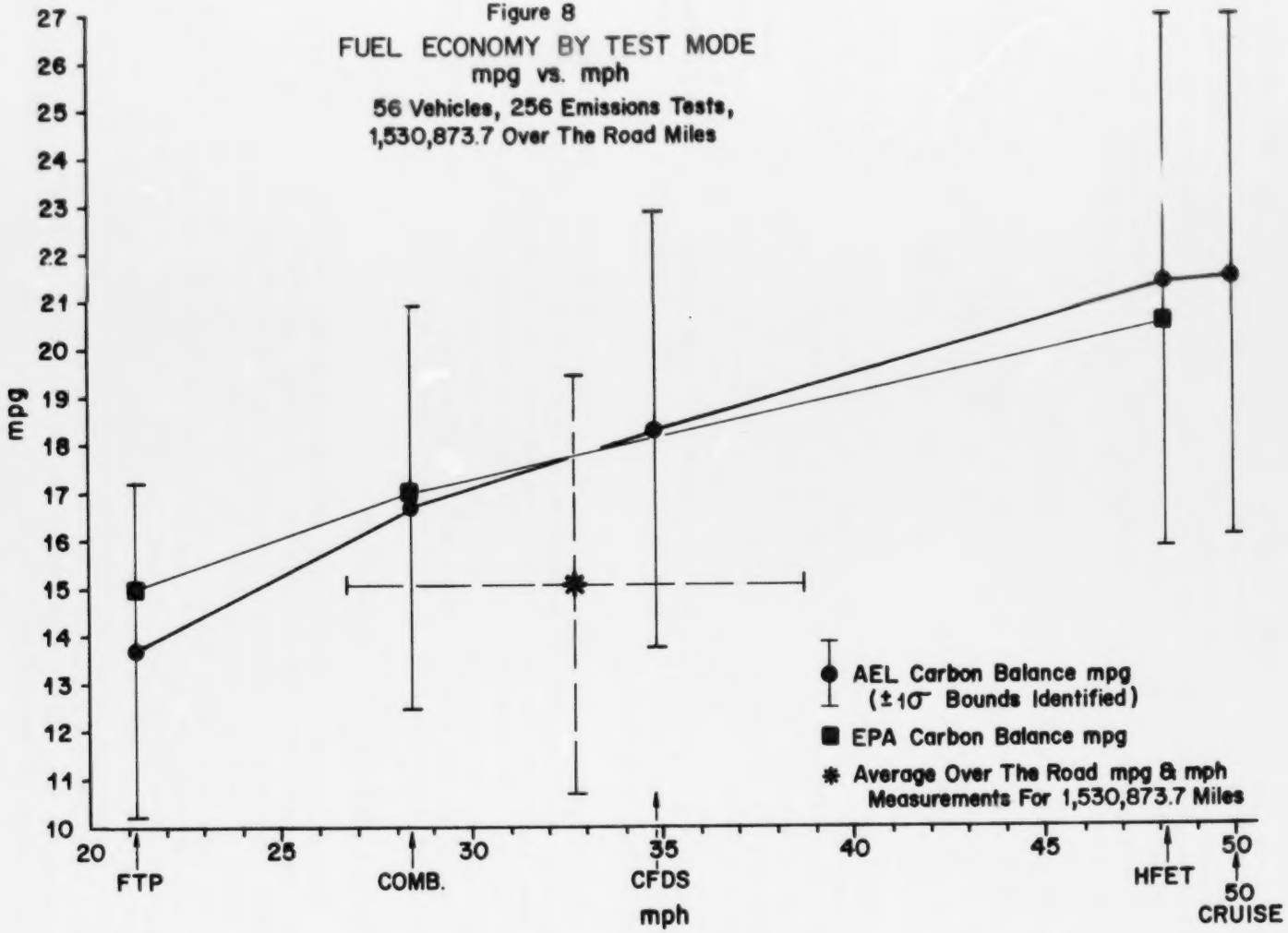


Figure 9

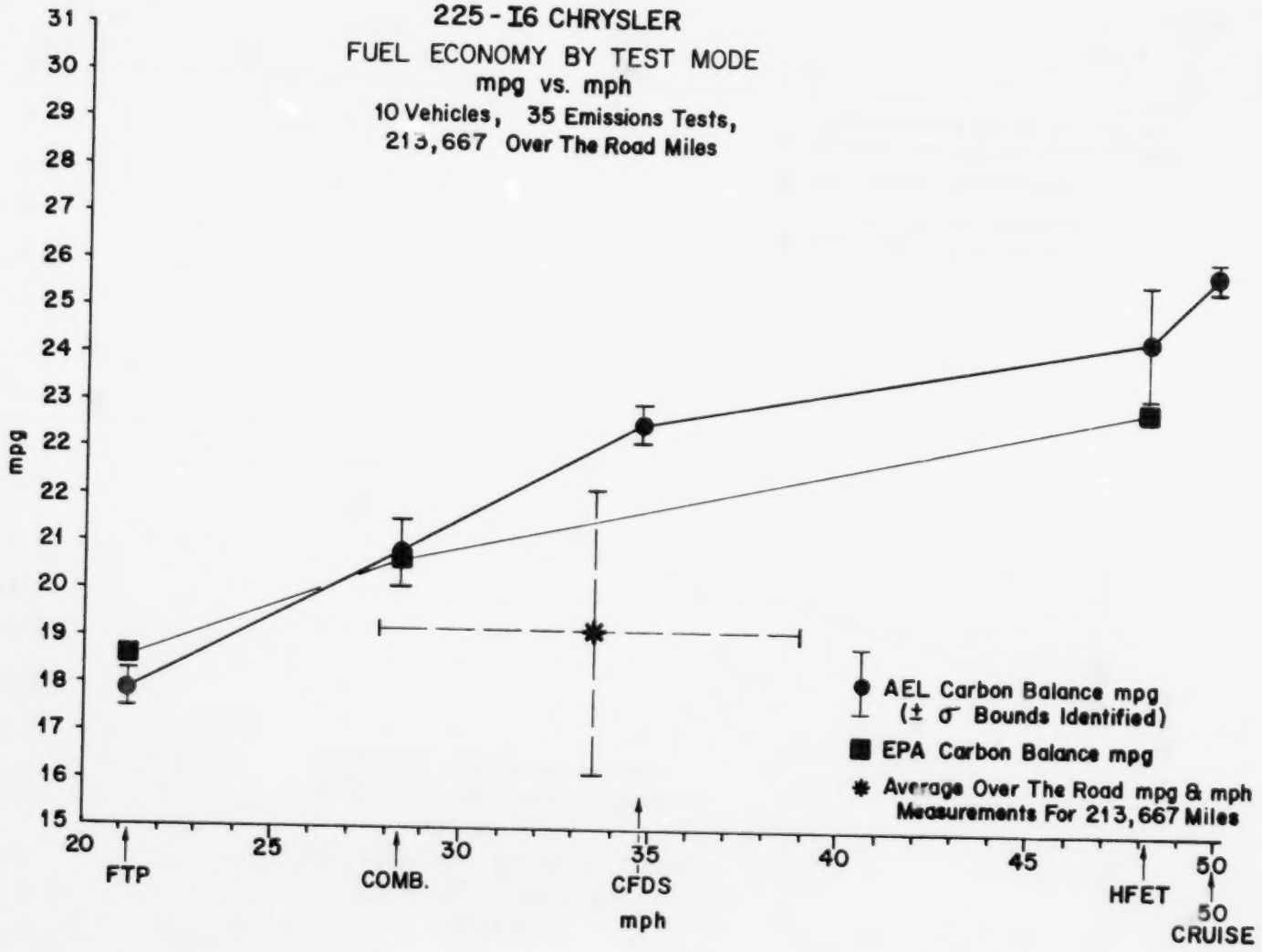

225 - I6 CHRYSLER
FUEL ECONOMY BY TEST MODE
mpg vs. mph
10 Vehicles, 35 Emissions Tests,
213,667 Over The Road Miles
mpg
31
30
29
28
27
26
25
24
23
22
22
21
20
19
18
17
16
15
20
25
30
35
40
45
50
FTP
COMB.
CFDS
mph
HFET
50
CRUISE
AEL Carbon Balance mpg
(± σ Bounds Identified)
EPA Carbon Balance mpg
Average Over The Road mpg & mph
Measurements For 213,667 Miles

Figure 10

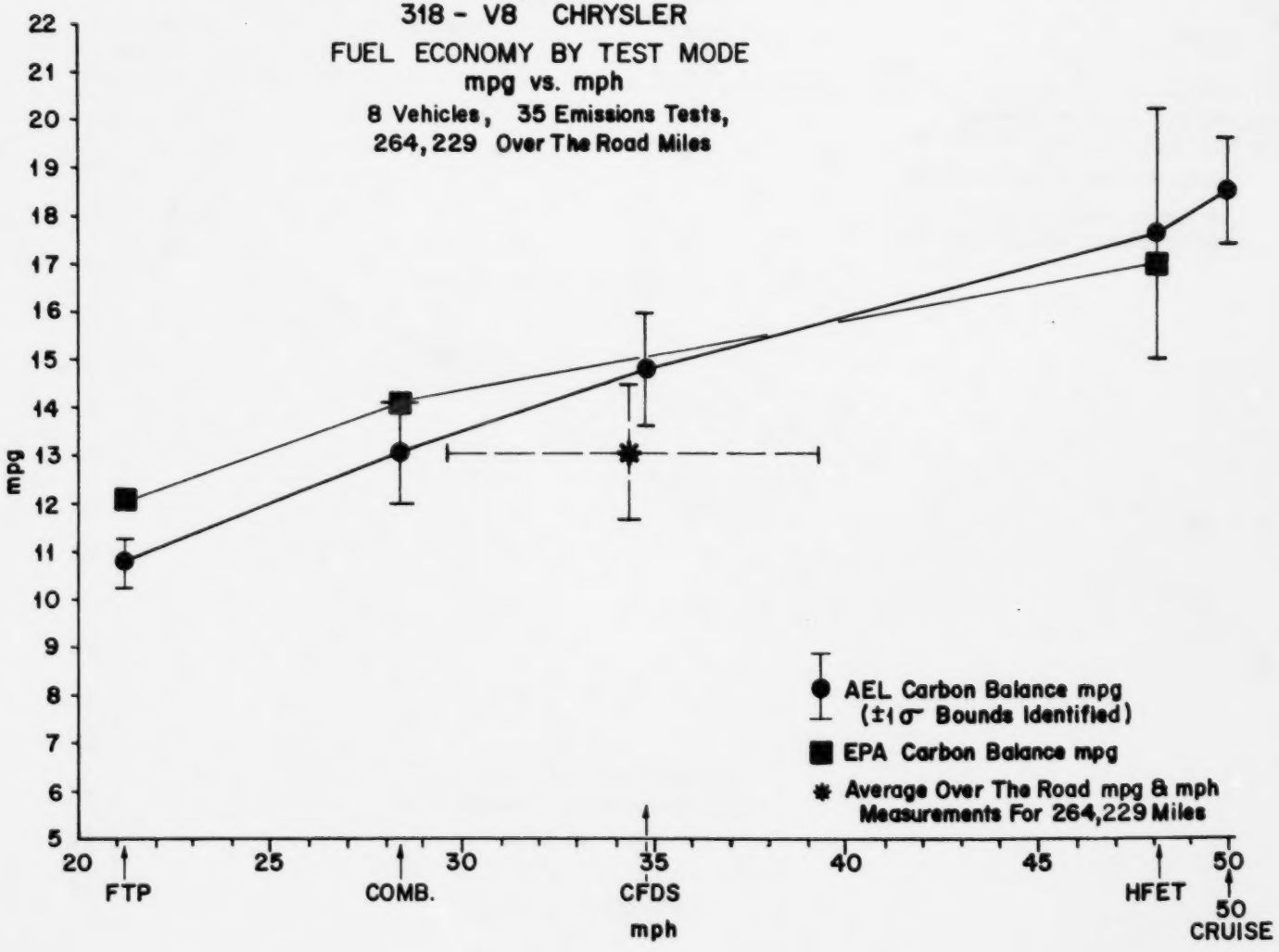

318 - V8 CHRYSLER
FUEL ECONOMY BY TEST MODE
mpg vs. mph
8 Vehicles, 35 Emissions Tests,
264,229 Over The Road Miles
mpg
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
20
25
30
35
40
45
50
FTP
COMB.
CFDS
HFET
50
CRUISE
mph
AEL Carbon Balance mpg
(±1σ Bounds Identified)
EPA Carbon Balance mpg
Average Over The Road mpg & mph
Measurements For 264,229 Miles

Figure 11

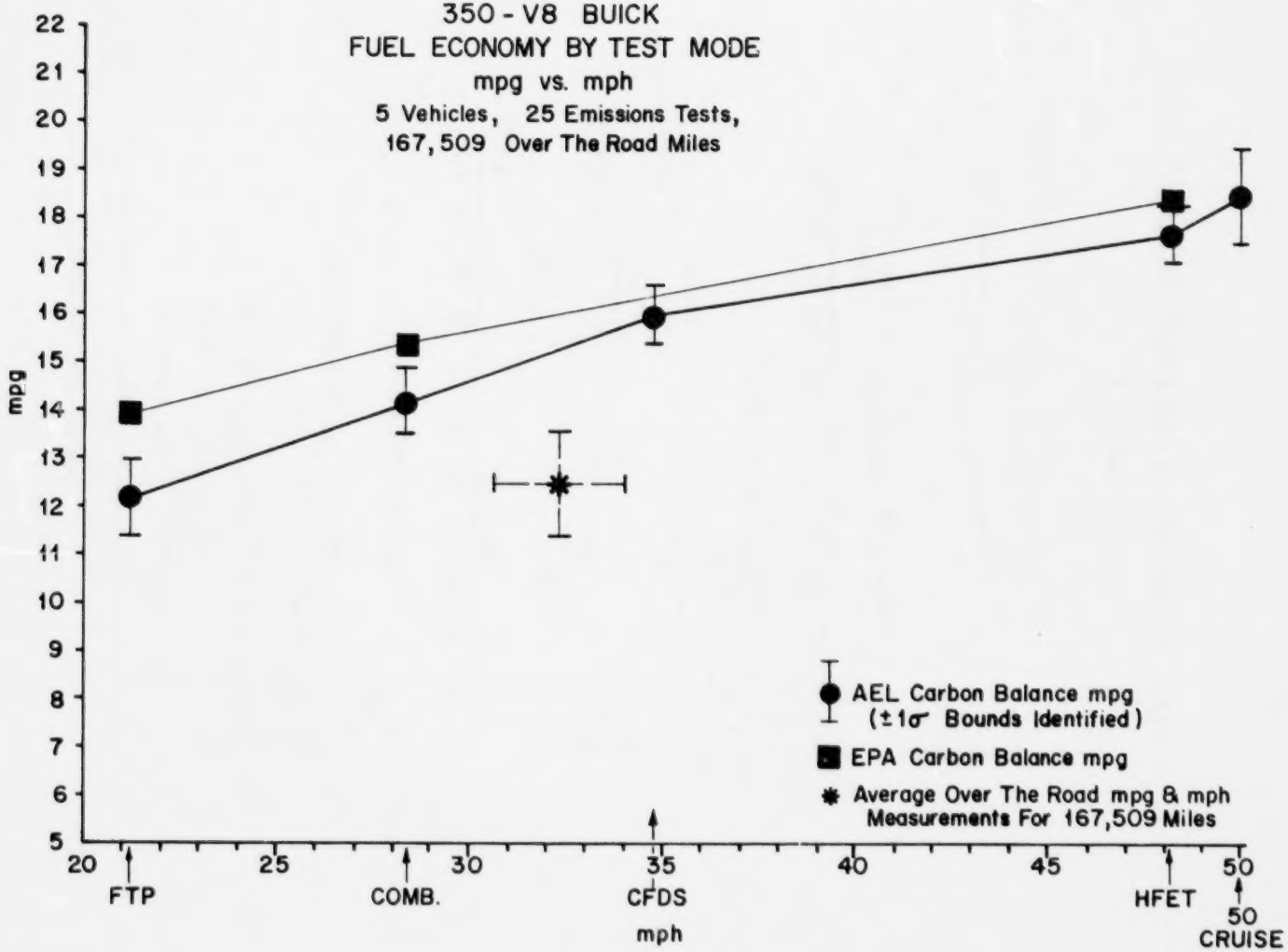
350 - V8 BUICK

FUEL ECONOMY BY TEST MODE

mpg vs. mph

5 Vehicles, 25 Emissions Tests,

167,509 Over The Road Miles



FUEL ECONOMY vs MILEAGE ACCUMULATION

Figure 12. CAR NO. 2

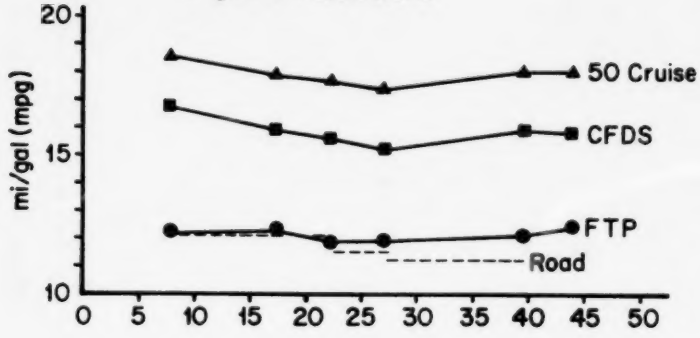


Figure 13. CAR NO. 19

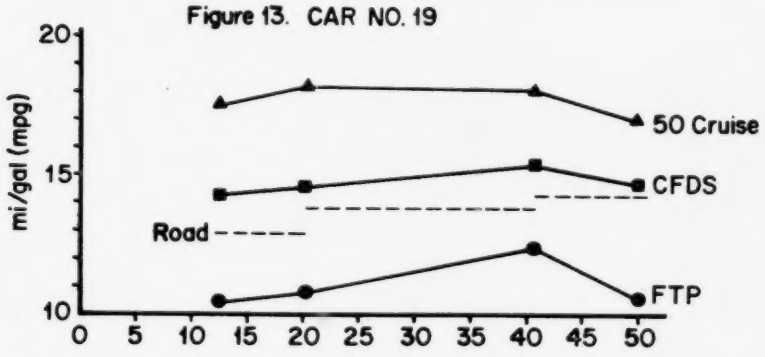


Figure 14. CAR NO. 25

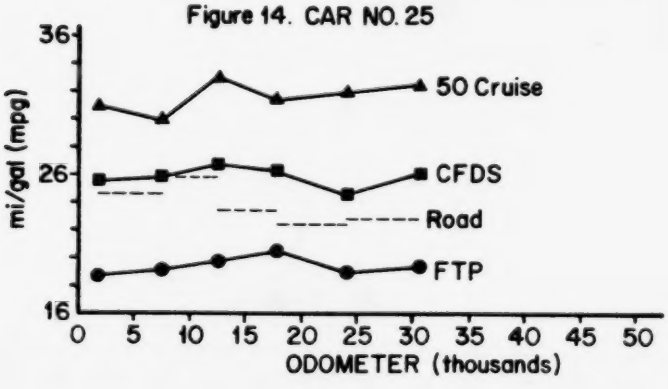
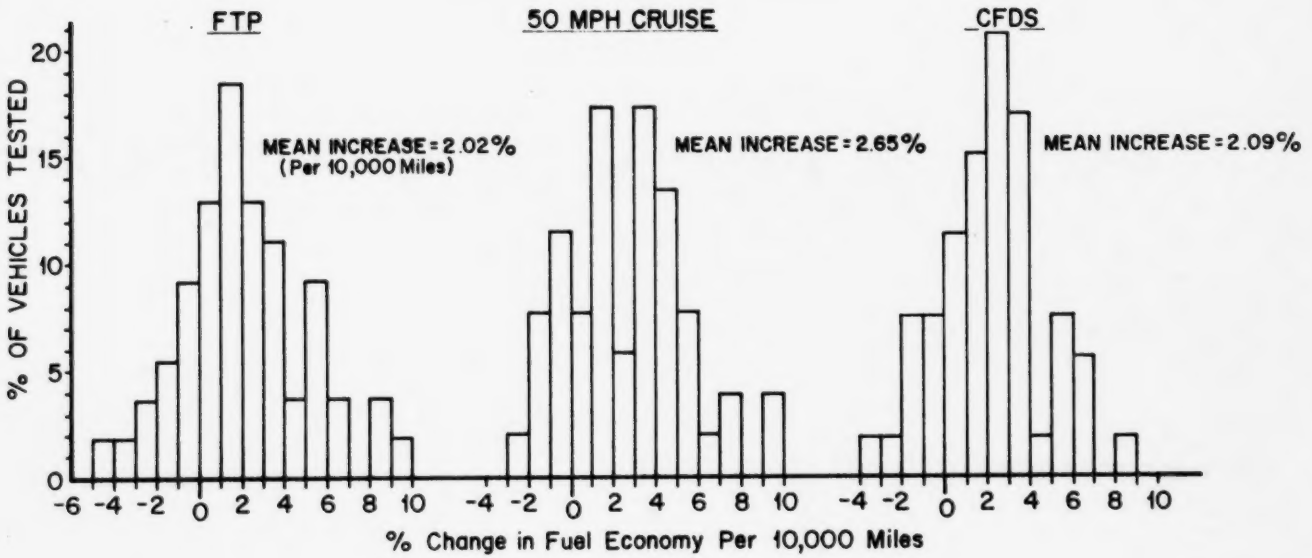


Figure 15
MILEAGE ACCUMULATION TRENDS FOR
CARBON BALANCE FUEL ECONOMY
TOTAL VEHICLE SAMPLE GROUP



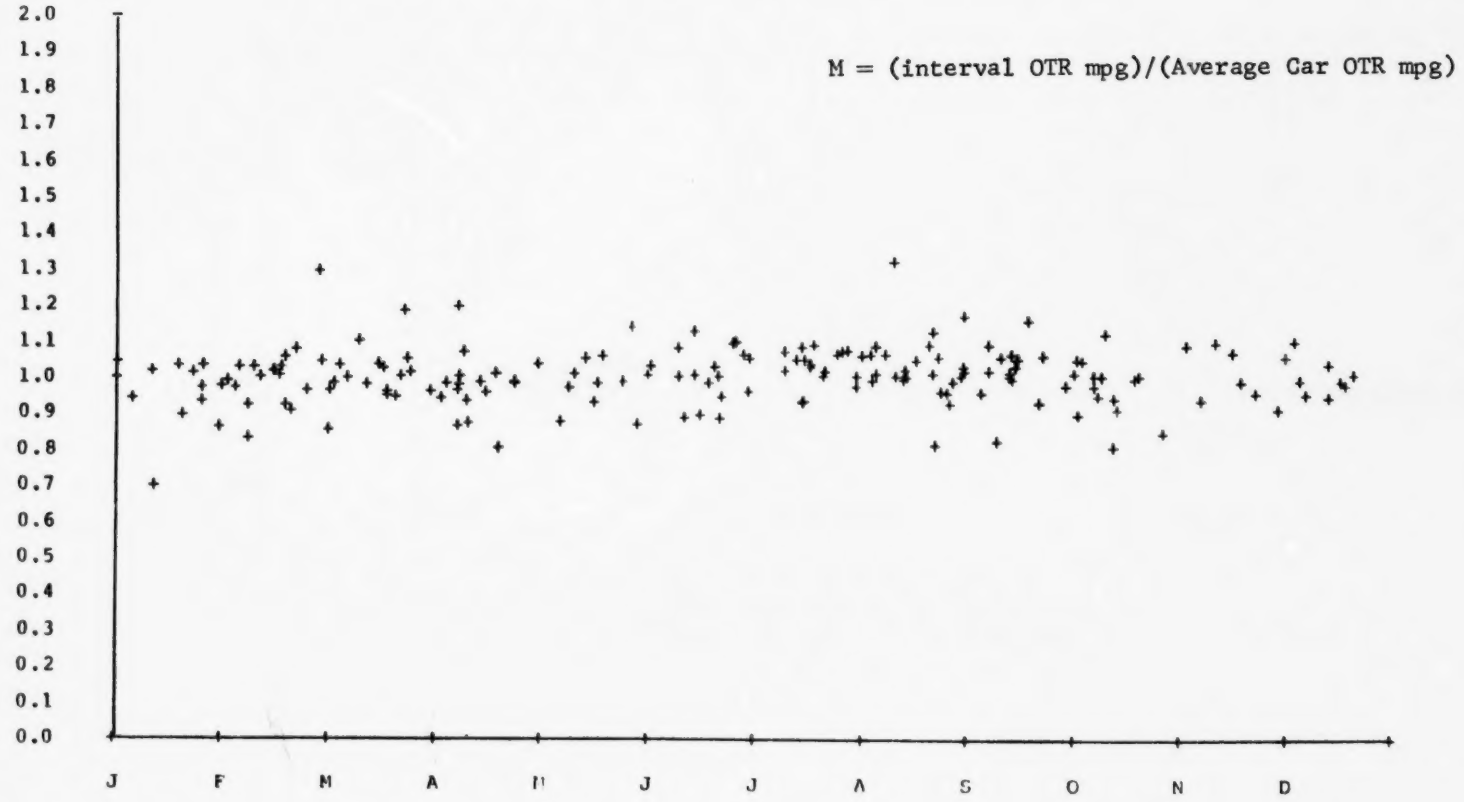


Figure 16. Seasonal OTR Fuel Economy.

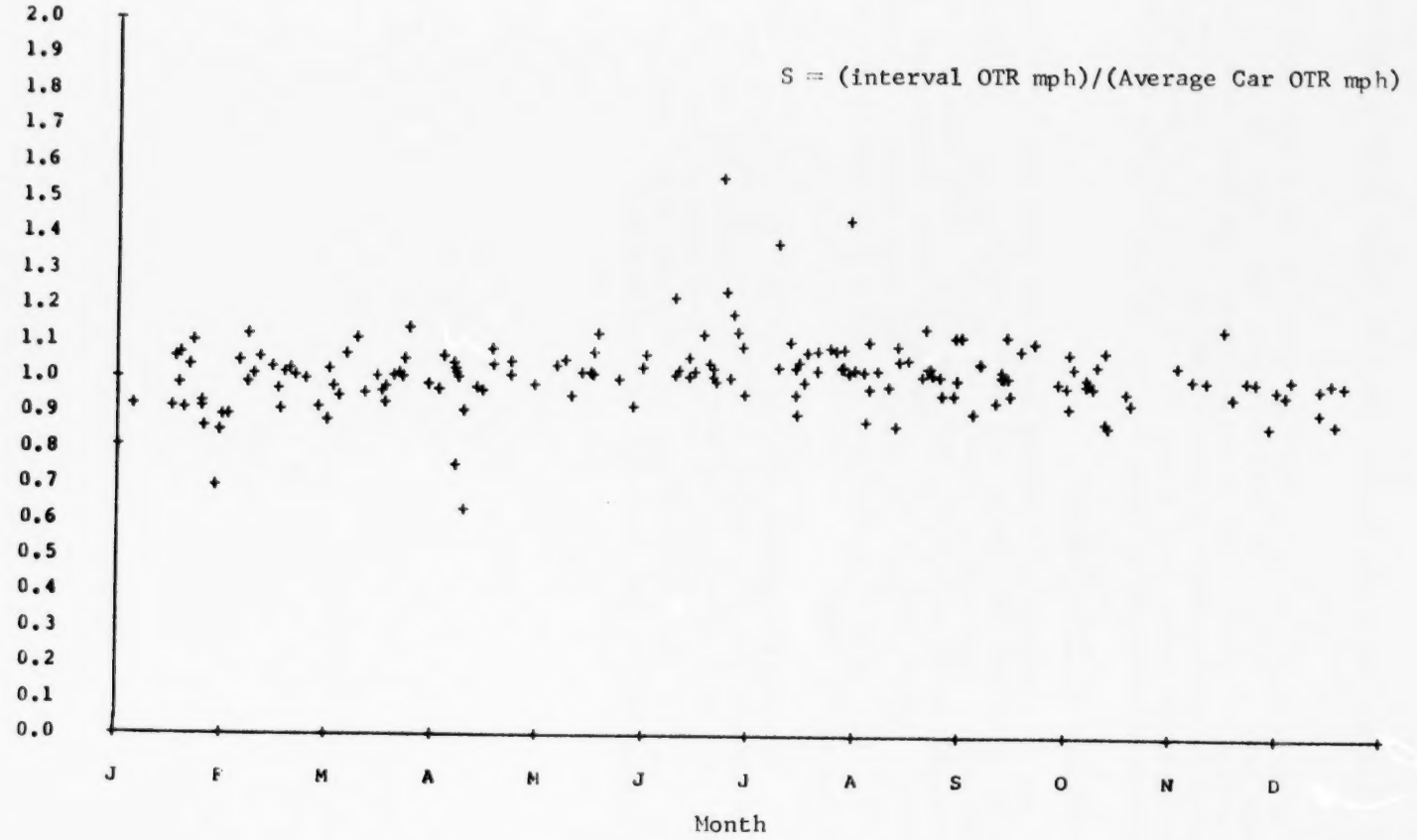


Figure 17. Seasonal OTR Vehicle Speed

speed from all intervals is also shown in Figure 18 as a cumulative frequency plot.

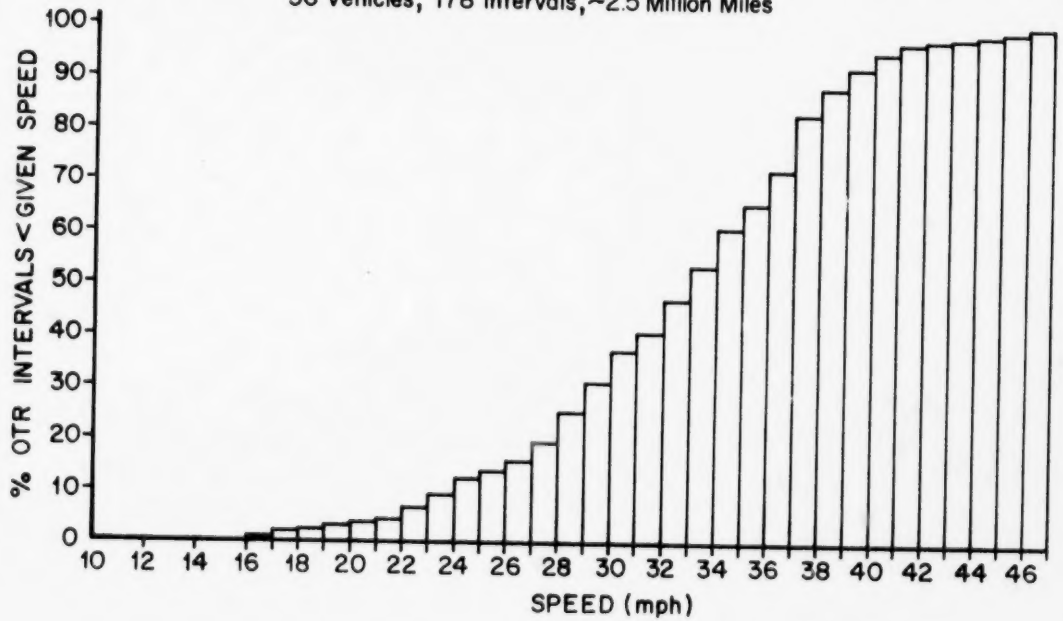
Several analyses were performed to establish a relationship between vehicle inertia weight and fuel economy. While inertia weight had a significant effect on fuel economy in comparisons among individual cars, the wide range of results at any one inertia setting and the limited weight range representation in the test group did not support any conclusions quantifying a general relationship between fuel economy and vehicle inertia weight.

Control Vehicle Fuel Economy

OTR fuel economy and vehicle speed are available for the project control vehicle (# 1) for every tank fill in the course of the study, spanning over 30,000 miles. The control vehicle was fueled exclusively from a 1,000 gallon tank at AEL using commercial lead free fuel. These data are for much shorter time and distance intervals than the 5,000 mile test interval values used for the calculation of other test vehicle OTR fuel economy. Figures 19 and 20 show OTR fuel economy and average speed for this vehicle for each tank fill by month of the year.

In Figure 19 a gradual seasonal fuel economy shift is noticeable during the warmer months. Each point in Figure 19 represents at most a few hundred miles and a time period of not more than a week. This allows the data to be more sensitive to factors such as type of usage, weather and road conditions, etc., than for the OTR intervals on other test group cars where each interval represents about 5,000 miles and several months.

Figure 18
CUMULATIVE FREQUENCY DISTRIBUTION
OTR VEHICLE SPEED
56 Vehicles, 178 Intervals, ~2.5 Million Miles



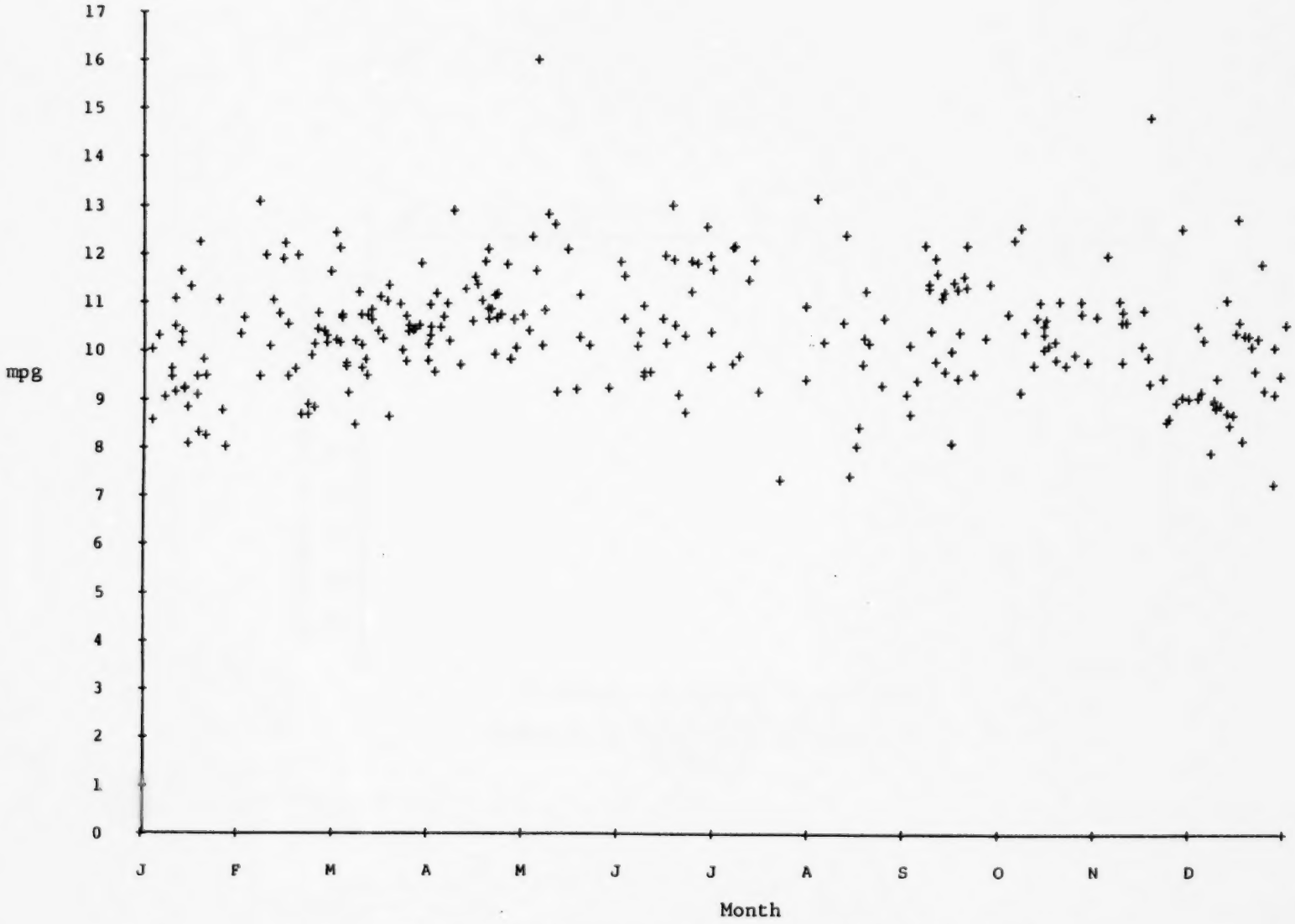


Figure 19. Seasonal OTR Fuel Economy for Control Vehicle.

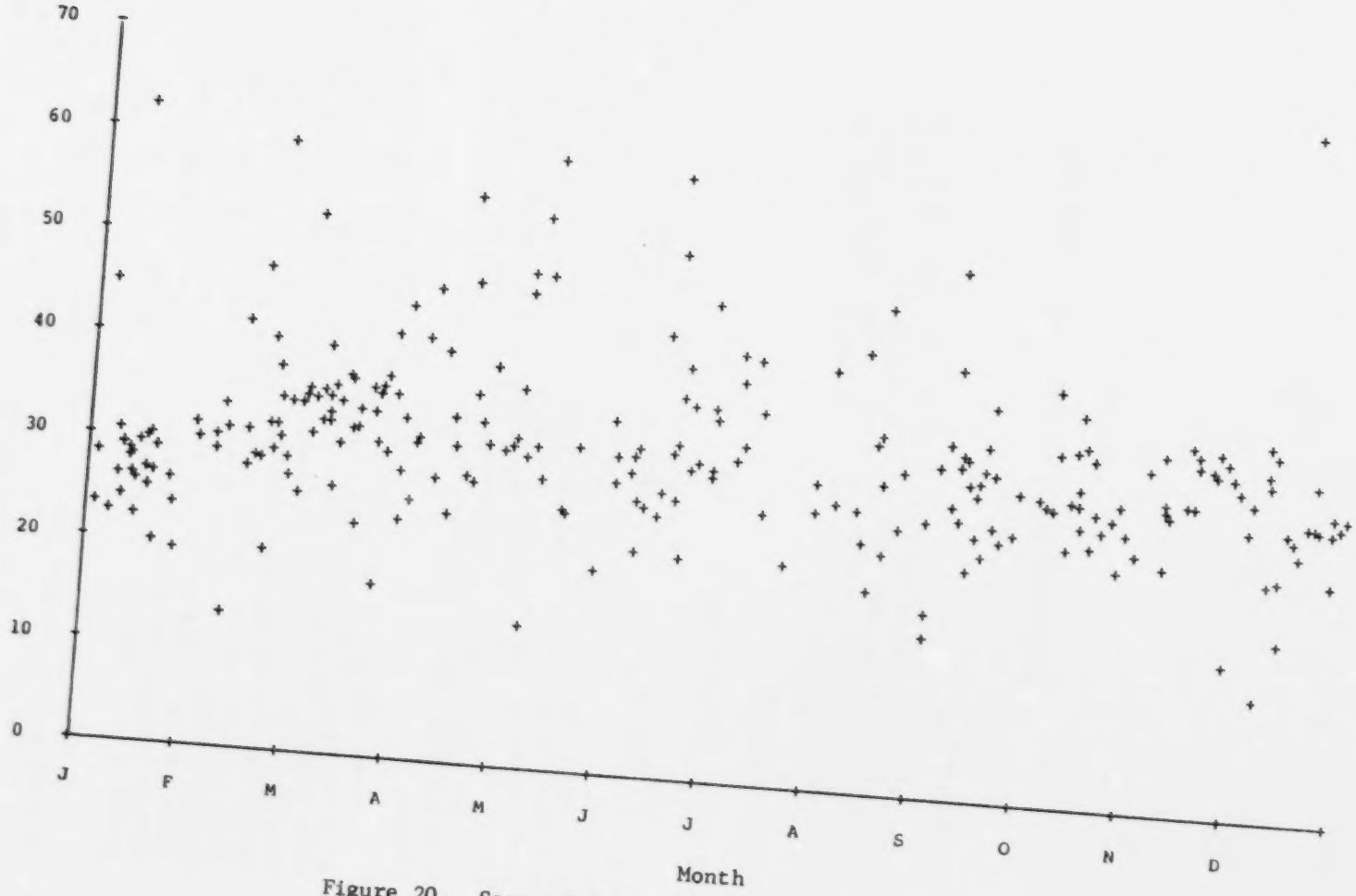


Figure 20. Seasonal OTR Vehicle Speed for Control Vehicle.

SECTION 5

CHARACTERIZATION OF PARTICULATE EMISSIONS

INTRODUCTION

Particulate samples were analyzed for sulfate content as one of the key objectives of the project, and these emission rates have been presented in Section 3. Additional analyses provide a more complete characterization of the particulate emissions for these cars and are included in this section.

SULFATE EMISSIONS

Stabilized CFDS Sulfate Emissions

Previous studies (1-8) of sulfate production from catalyst-equipped vehicles have shown that the efficiency of conversion of fuel sulfur to sulfate particulate is dependent on catalyst type (monolith or beaded) and the presence or absence of an air pump. Measurement of sulfate particulate emissions from catalyst-equipped cars is complicated by storage and release of sulfur-bearing compounds from the catalyst. Early studies of prototype cars (2, 15, 16, 17) frequently showed large variations in observed emission rates from the same vehicle in series of back-to-back tests. Therefore, five consecutive CFDS cycles were used in order to insure representative CFDS sulfate values.

After 155 tests, analysis of the five CFDS cycles yielded fairly consistent patterns of sulfate emissions for three of the four possible catalyst/air pump configurations. The five CFDS sulfate emission rates were individually averaged over all tests representing each configuration to ascertain a composite pattern of sulfate emissions variation for the given system configuration. These results are shown in Figures 21, 22, and 23 for the following configurations: 1) monolith without air pump, 73 tests; 2) monolith with air pump, 22 tests; and 3) beaded without air pump, 51 tests. Since only 9 tests on two vehicles comprised the last configuration, beaded with air pump, this group was not analyzed for emission variations.

Examination of cycle 1 sulfate averages for the monolith without air pump configuration reveals cycle 1 sulfate emission rates which are significantly higher than the average of cycles 3, 4, and 5. Indeed, almost half of the tests on vehicles with this configuration exhibit cycle 1 emissions which are greater than the above average value by more than three times the standard

SULFATE EMISSIONS FOR CFDS CYCLES

Figure 21. MONOLITH CATALYST WITHOUT AIR PUMP

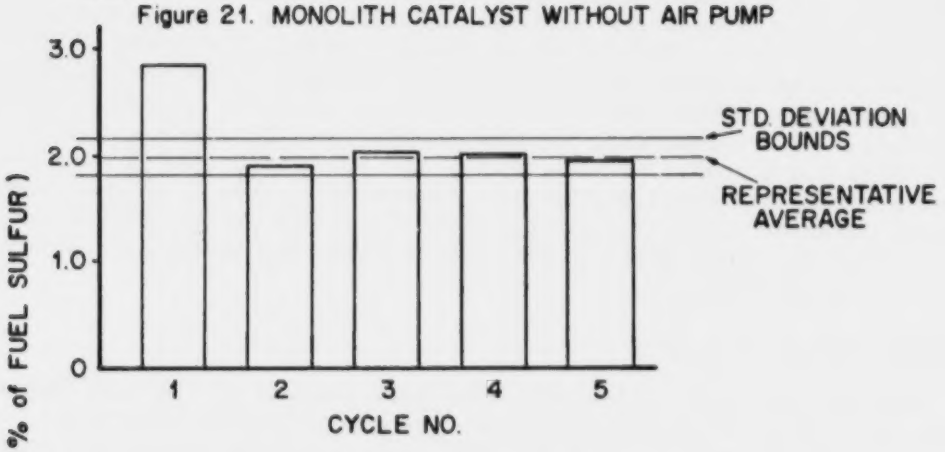


Figure 22. MONOLITH CATALYST WITH AIR PUMP

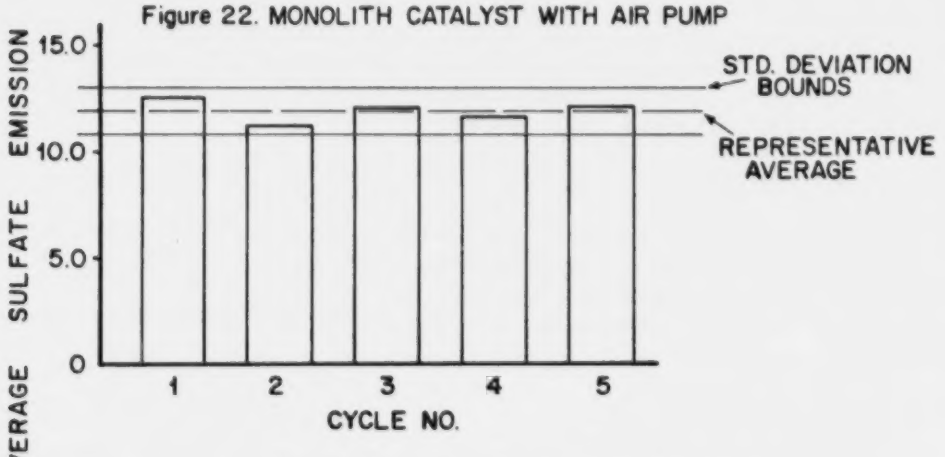
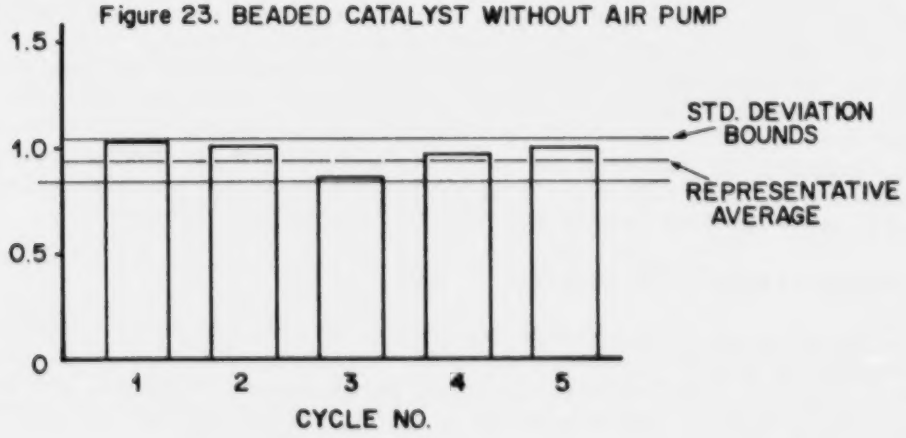


Figure 23. BEADED CATALYST WITHOUT AIR PUMP



deviation. As seen in Figures 22 and 23, there appears to be little "memory" of previous test cycles for the monolith with air pump and beaded without air pump configurations. For all three configurations, the second CFDS cycle gives an average sulfate value within the standard deviation bounds defined by the last three CFDS cycles. Therefore, in order to simplify test protocol while still maintaining data integrity, only two CFDS cycles were run for tests #163 and beyond. On this basis, all individual vehicle sulfate emission rates presented in Section 3 are the second CFDS value. Detailed analysis of sulfate emission rates in Sections 5 and 7 use the second CFDS value for tests after #162; for tests where 5 CFDS cycles exist the average of the last 3 cycles were employed.

Sulfate Emissions at Idle

Two filters were collected during idle periods of the test sequence for tests up to and including test #162. One was collected during the 5-minute idle separating the 50 mph cruise from the first CFDS cycle, the other was a composite sample from idle periods after CFDS cycles 3, 4, and 5. BCA analysis of these filters showed low levels of sulfate emissions during idle operation. When a driving cycle and its associated idle period were combined, less than 2% of the sulfate collected and 0.2% of the fuel sulfur recovery could be attributed to the idle period.

Sulfate Emission Rates

Sulfate emissions as percent of fuel sulfur recovery are presented in Table 13. All emission rates have been normalized to 0.030 wt % S using actual fuel sulfur values provided by fuel analysis. Fuel sulfur content, as well as fuel lead and manganese, are indicated in Figure 24 as three month running averages.

TOTAL PARTICULATE MASS

Total particulate mass was determined for every filter collected. Particulate from the cold-start FTP usually appeared as a black carbon-like deposit, while the CFDS and 50 mph cruise tests showed a tan or white particulate. Sulfate emissions from the FTP were lower than for the CFDS or 50 mph cruise. Table 14 gives total particulate mass, averaged over all tests on each car, for the FTP, CFDS, and 50 mph cruise segments. The percentage of this particulate found to be sulfate is indicated for each segment. Also presented in this table are comparisons of relative emission rates of total particulate in CFDS and 50 mph cruise relative to FTP results.

ELEMENTAL PARTICULATE ANALYSIS BY XRF

Particulate samples from the 1-hour 50 mph cruise were analyzed for 10 elements by x-ray fluorescence (XRF). Elements analyzed were: bromine, lead, zinc, copper, iron, sulfur, calcium, phosphorous, aluminum, and manganese. The 1-hour cruise was adopted in order to collect sufficient particulate for

Table 13

Sulfate Emissions as % of Fuel
Sulfur Recovery By
Catalyst/Air Pump Configuration

Configuration	# Tests	Fuel Sulfur Recovery as Sulfate(%)				Sulfate Emission Rate (mg/mi)			
		FTP	50 Cruise	CFDS	HFET	FTP	50 Cruise	CFDS	HFET
Monolith without Air Pump	124	0.82	6.31	1.98	2.79	1.72	8.08	3.21	3.58 (24)
Monolith with Air Pump	39	2.33	14.26	14.18	36.33	4.29	17.20	18.70	31.33 (8)
Beaded without Air Pump	80	0.50	1.58	0.94	2.14	0.89	2.03	1.32	2.75 (11)
Beaded with Air Pump	16	0.60	6.32	6.00	15.74	1.34	10.16	10.18	25.49 (5)
All Tests	259	0.94	6.04	3.74	7.24	1.83	7.71	5.39	10.30 (44)

Note: All sulfate emission rates normalized to 0.030 weight percent sulfur in fuel.

For HFET # of tests are indicated in parentheses.

Figure 24

FUEL ANALYSES

THREE MONTH RUNNING AVERAGES

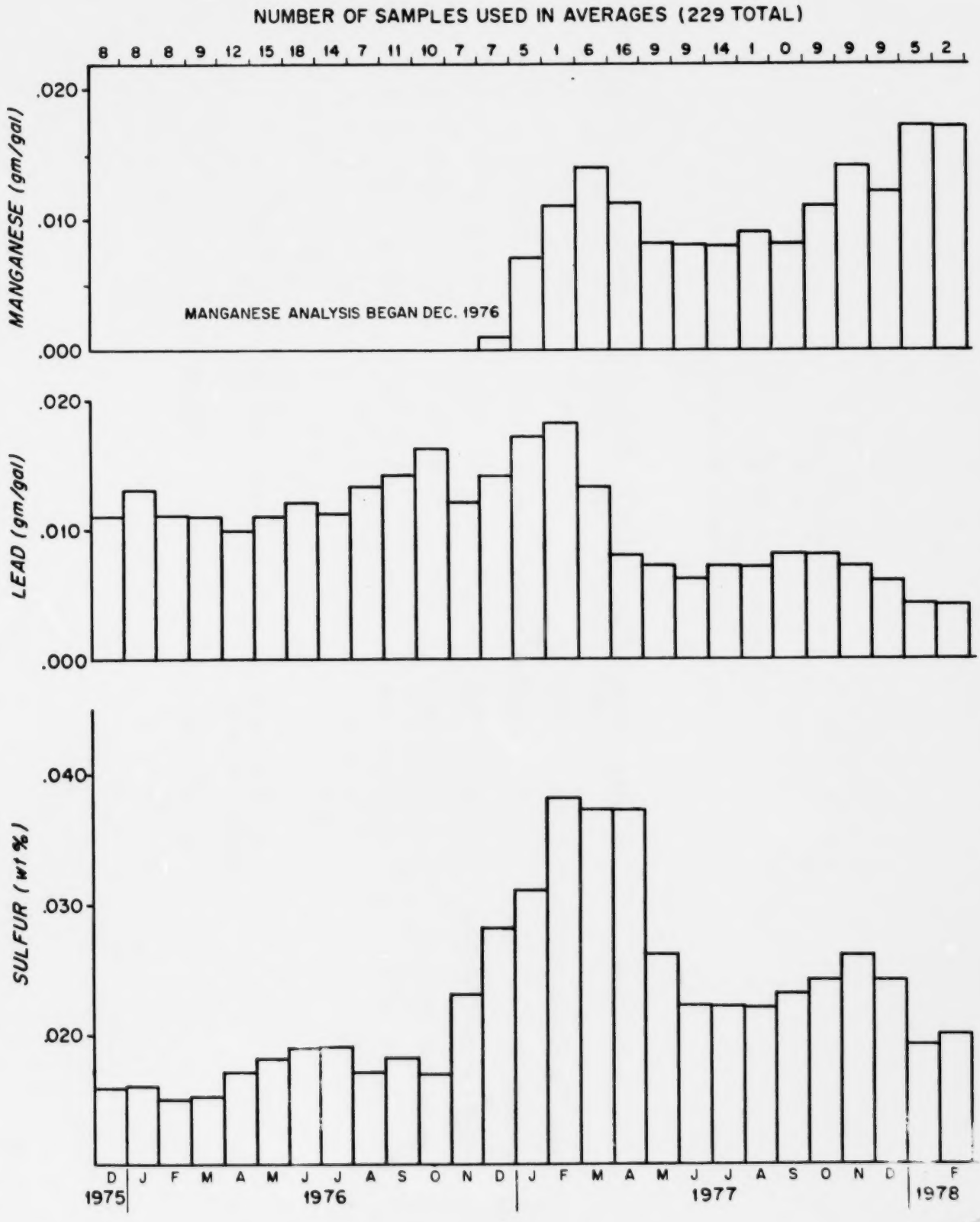

NUMBER OF SAMPLES USED IN AVERAGES (229 TOTAL)
8 8 8 9 12 15 18 14 7 11 10 7 7 5 1 6 16 9 9 14 1 0 9 9 9 5 2
MANGANESE (gm/gal)
.020
.010
.000
MANGANESE ANALYSIS BEGAN DEC. 1976
LEAD (gm/gal)
.020
.010
.000
SULFUR (wt %)
.040
.030
.020
D J F M A M J J A S O N D J F M A M J J A S O N D F
1975
1976
1977
1978

Table 14

Total Particulate Emissions By Car

		Total Particulate mg/m			TP; % of FTP		% TP as SO4		
CAR#	# of Tests	FTP	50C	CFDS	50C	CFDS	FTP	50C	CFDS
1	11	22.82	10.81	13.01	47.37	57.03	8.56	91.25	68.93
2	6	10.70	1.88	1.88	17.58	17.62	3.31	14.45	12.61
3	7	10.90	5.05	2.27	46.36	20.83	9.40	63.77	57.72
4	5	43.88	4.23	4.16	9.65	9.48	1.63	31.00	40.28
5	4	54.28	4.12	4.59	7.59	8.45	2.19	9.83	4.71
6	4	3.78	1.92	2.49	50.85	65.90	13.72	54.64	44.35
7	5	15.81	3.70	4.60	23.40	29.10	2.43	60.25	12.92
8	5	8.34	11.77	14.67	141.20	175.94	16.05	90.57	50.23
9	5	37.65	12.70	5.75	33.73	15.27	3.84	53.54	61.43
10	5	25.41	4.84	2.53	19.04	9.95	3.87	78.66	43.37
11	5	37.71	6.25	3.19	16.57	8.46	1.53	53.48	28.97
12	5	36.99	8.25	12.57	22.30	33.98	5.80	65.06	66.88
13	10	26.95	4.40	4.19	16.32	15.55	3.17	55.97	16.61
14	2	9.14	6.46	11.17	70.66	122.18	7.92	52.59	9.44
15	4	52.31	8.47	6.35	16.20	12.14	2.34	65.16	20.23
16	3	53.16	6.18	7.75	11.62	14.58	1.56	55.07	76.66
17	5	5.13	6.10	4.22	118.90	82.25	18.64	85.88	116.90
18	5	36.17	12.54	6.81	34.67	18.82	10.54	82.99	48.76
19	4	34.24	13.52	8.73	39.49	25.50	6.41	100.85	61.93
20	5	26.77	7.59	4.64	28.34	17.35	9.25	69.01	57.49
21	5	44.35	5.18	4.75	11.67	10.71	3.34	29.87	10.99
22	4	4.24	0.79	1.10	18.53	25.89	15.56	19.36	25.64
23	6	31.88	4.58	2.78	14.36	8.73	2.66	76.33	23.79
24	2	10.89	9.89	3.23	90.82	29.63	9.02	87.70	70.44
25	6	11.57	11.81	13.68	102.12	118.32	9.45	66.64	62.34
26	4	41.46	13.95	23.74	33.64	57.24	8.26	45.02	32.80
27	5	32.47	7.34	9.29	22.61	28.61	3.74	5.93	5.07
28	5	3.62	1.34	1.73	37.10	47.65	20.44	41.41	37.16
29	4	11.51	1.63	3.16	14.15	27.48	4.57	33.26	17.12
30	4	4.72	1.41	2.33	29.94	49.33	5.35	41.94	14.01
31	4	11.20	10.22	9.36	91.30	83.62	5.81	38.58	10.00
32	5	10.09	0.80	3.75	7.89	37.11	3.31	26.81	13.37
33	3	12.04	14.62	7.76	121.45	64.44	7.00	11.25	7.36
34	5	22.38	18.41	4.34	82.29	19.38	2.77	79.33	14.23
35	5	17.96	22.19	6.79	123.54	37.80	8.70	75.71	50.92
36	5	13.87	10.30	5.61	74.25	40.42	3.14	66.89	17.52
37	3	6.92	1.67	5.85	24.11	84.58	6.42	39.70	11.23
38	6	7.55	4.93	3.71	65.26	49.13	2.91	44.02	31.69
39	3	5.78	3.34	4.15	57.81	71.84	7.74	36.33	71.00
40	2	10.98	4.82	2.04	43.92	18.54	4.70	67.88	23.29
41	4	8.07	2.12	6.67	26.24	82.63	4.86	14.87	34.27
42	4	55.35	8.76	9.24	15.82	16.70	1.20	60.04	17.61
43	4	24.38	7.33	9.08	30.07	37.24	2.93	38.31	6.63
44	3	35.49	20.64	28.79	58.70	81.11	8.86	88.82	56.21
45	4	10.86	10.88	9.85	100.25	90.74	25.41	38.36	33.80
46	5	15.75	13.77	12.26	87.44	77.83	16.50	45.12	40.07
47	4	21.33	10.60	14.97	49.70	70.17	9.07	41.47	37.77
48	4	9.05	1.98	2.42	21.83	26.72	7.05	27.08	34.82
49	3	7.98	9.08	3.42	113.79	42.84	5.45	65.26	26.44
50	3	6.96	6.92	4.39	99.42	63.13	10.56	79.01	24.54
51	5	4.18	4.70	3.26	112.40	78.04	19.14	48.11	36.26
52	3	17 68	30.19	34.71	170.78	196.36	18.15	94.80	91.97
53	8	14.23	10.95	5.17	77.00	36.31	10.29	60.84	28.26
54	4	5.74	1.87	1.92	32.53	33.46	13.79	25.62	37.13
55	3	76.28	11.91	36.47	15.62	47.81	1.82	4.88	2.43
56	3	33.97	18.47	15.45	54.38	45.48	13.46	37.53	40.85
AVERAGE		21.70	8.22	7.91	51.87	48.17	7.78	52.47	35.70

detection since emission rates were expected to be very low. Detection limits ($\mu g/cm^2$ of filter area) for the XRF system are shown in Table 15. Translation of these detection limits to $\mu g/mi$ for typical 1-hour-50 mph cruise sampling conditions are also shown in Table 15. In addition, Table 15 lists the percentage of tests with samples below the XRF detection limit for each element. Table 16 is a tabulation of individual car average particulate elemental emissions. No trend with mileage accumulation was observed for elements analyzed. Histograms in Figures 25-34 illustrate the distribution of observed emissions. Tests with non-detectable emissions have been excluded from these histograms and the number of exclusions indicated on each figure.

For lead, sulfur and manganese, the particulate emitted can be compared to the fuel input for each element during the 50 mph cruise. Recoveries of these elements based on fuel usage were low. Lead and manganese are probably trapped in the catalyst and engine/exhaust system. Most fuel sulfur is emitted as SO_2 and little is found as particulate sulfur. Figures 35, 36, and 37 are histograms of the individual test particulate recovery percentages for sulfur, lead, and manganese, respectively.

PARTICULATE ANALYSIS BY ION CHROMATOGRAPHY (IC)

At the end of the study, ion chromatography (23) was used to analyze the archived filters previously used for XRF analysis. Anions determined by IC were Cl^-, Br^-, $PO_4^{\equiv}$, F^-, and NO_3^-, in water soluble extracts of particulate. Chromatographs of these filter extracts showed low levels of the ions analyzed. Section 8 contains a comparison of the results of the BCA, XRF and IC analyses for sulfur and sulfate. In Table 17 the total particulate mass emission rate during the 50 mph cruise is broken down into a sulfate (based on XRF sulfur), XRF non-sulfate, IC non-sulfate and "remainder" contributions. When sulfate, XRF non-sulfate, and IC detected species are combined, they account for approximately 65% of the total mass of emitted particulate regardless of the various sub-classifications listed in Table 17. These findings are in general agreement with results from similar work at Southwest Research Institute (14).

Table 15

XRF Detection Limits

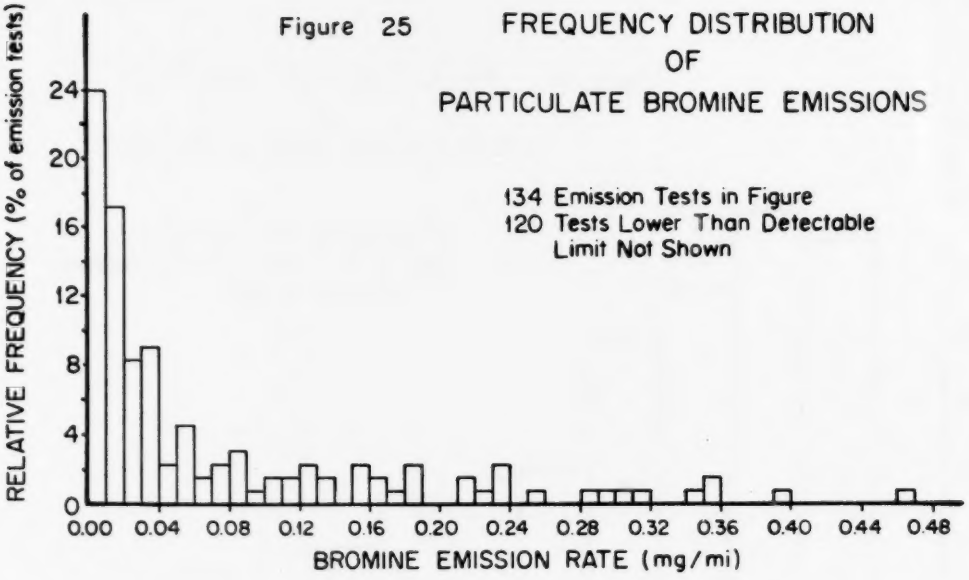
	ELEMENT									
	Br	Pb	Zn	Cu	Fe	S	Ca	P	Al	Mn
Lower limit of detection by calibration standard (microgram/cm^2 of exposed filter area)	0.05	0.1	0.2	0.2	0.05	0.025	0.008	0.09	0.07	0.011
Same as above translated to typical 1 hr. 50 mph cruise (micrograms/mi.)	2.2	4.4	8.8	8.8	2.2	1.1	0.4	4.0	3.1	0.5
% of tests lower than detection limit	47	27	74	91	71	2	33	24	92	67

Table 16. Average XRF Emissions by Car

Car	Tests	Miles Tested	Br	Pb	Zn	Cu	Fe	S	Ca	P	Al	Mn
1	11	29376.6	0.00	0.03	0.04	0.02	0.01	2.19	0.19	0.17	0.00	0.00
2	6	36267.7	0.32	0.01	0.01	0.01	0.01	0.05	0.00	0.01	0.00	0.00
3	7	41869.1	0.04	0.01	0.01	0.01	0.01	1.20	0.04	0.09	0.00	0.00
4	5	31633.6	0.03	0.01	0.00	0.02	0.02	0.36	0.03	0.03	0.00	0.00
5	4	12629.7	0.21	0.02	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.00
6	5	33719.4	0.01	0.01	0.00	0.00	0.00	0.37	0.02	0.01	0.00	0.00
7	5	33904.9	0.00	0.02	0.01	0.00	0.00	0.63	0.04	0.04	0.00	0.00
8	5	30134.9	0.01	0.11	0.00	0.00	0.04	2.68	0.05	0.05	0.00	0.00
9	5	37276.5	0.01	0.04	0.04	0.00	0.03	1.67	0.08	0.10	0.01	0.0
10	5	30509.2	0.02	0.01	0.00	0.01	0.00	0.96	0.02	0.02	0.00	0.00
11	5	37666.3	0.03	0.02	0.01	0.01	0.00	1.18	0.03	0.04	0.00	0.00
12	4	28771.4	0.00	0.01	0.00	0.01	0.01	1.43	0.02	0.02	0.00	0.00
13	10	54719.9	0.08	0.03	0.04	0.00	0.03	0.68	0.08	0.18	0.00	0.00
14	2	7828.1	0.01	0.10	0.00	0.00	0.01	0.66	0.00	0.02	0.00	0.00
15	4	28799.9	0.01	0.02	0.00	0.00	0.00	1.48	0.04	0.04	0.00	0.00
16	3	37876.2	0.01	0.01	0.00	0.00	0.00	0.99	0.05	0.05	0.00	0.00
17	5	36202.9	0.00	0.02	0.01	0.01	0.01	1.70	0.00	0.02	0.01	0.00
18	5	32452.6	0.00	0.01	0.01	0.00	0.00	2.33	0.05	0.05	0.00	0.01
19	4	37367.3	0.00	0.02	0.01	0.04	0.00	3.57	0.07	0.07	0.00	0.00
20	5	40464.9	0.03	0.02	0.00	0.00	0.00	1.19	0.04	0.07	0.00	0.01
21	5	29052.6	0.01	0.01	0.01	0.00	0.00	0.84	0.04	0.07	0.00	0.00
22	3	10332.7	0.14	0.00	0.00	0.00	0.01	0.02	0.02	0.02	0.00	0.00
23	6	29438.2	0.00	0.01	0.00	0.00	0.00	1.05	0.03	0.03	0.00	0.00
24	2	3286.4	0.00	0.02	0.00	0.00	0.00	2.31	0.00	0.01	0.00	0.00
25	6	28704.0	0.00	0.01	0.00	0.01	0.00	1.79	0.03	0.03	0.00	0.01
26	4	12175.0	0.02	0.05	0.00	0.01	0.09	1.64	0.05	0.10	0.01	0.00
27	5	28067.9	0.14	0.04	0.00	0.00	0.00	0.03	0.10	0.12	0.00	0.01
28	5	19504.7	0.02	0.02	0.00	0.00	0.01	0.11	0.02	0.01	0.00	0.00
29	4	21752.3	0.00	0.02	0.00	0.00	0.01	0.16	0.02	0.02	0.01	0.00
30	4	17945.3	0.00	0.01	0.01	0.00	0.00	0.22	0.02	0.01	0.00	0.00
31	4	12093.4	0.25	0.32	0.05	0.00	0.02	0.75	0.07	0.13	0.01	0.01
32	5	37030.7	0.00	0.01	0.00	0.00	0.00	0.02	0.04	0.03	0.00	0.00
33	3	26560.4	0.05	0.08	0.01	0.00	0.05	0.23	0.03	0.05	0.00	0.00
34	5	24631.7	0.00	0.01	0.00	0.06	0.01	4.59	0.04	0.05	0.00	0.02
35	5	30863.5	0.00	0.01	0.01	0.01	0.00	4.37	0.05	0.07	0.00	0.01
36	5	31692.2	0.00	0.03	0.00	0.00	0.01	2.10	0.05	0.05	0.00	0.00
37	3	10944.2	0.02	0.02	0.00	0.00	0.01	0.15	0.01	0.01	0.00	0.00
38	6	30299.9	0.00	0.02	0.00	0.00	0.00	1.49	0.04	0.04	0.00	0.00
39	3	14162.5	0.13	0.04	0.01	0.01	0.00	0.12	0.01	0.03	0.00	0.00
40	2	4222.8	0.03	0.02	0.00	0.00	0.00	1.03	0.00	0.00	0.00	0.00
41	4	23585.9	0.02	0.02	0.01	0.00	0.01	0.01	0.05	0.05	0.02	0.01
42	4	22107.7	0.04	0.04	0.03	0.00	0.00	1.31	0.16	0.26	0.00	0.01
43	4	29336.8	0.04	0.02	0.01	0.00	0.00	0.86	0.07	0.07	0.00	0.00
44	3	13809.7	0.00	0.04	0.00	0.00	0.01	3.68	0.12	0.11	0.00	0.00
45	4	32284.9	0.00	0.05	0.01	0.01	0.01	1.05	0.03	0.03	0.00	0.00
46	5	27135.4	0.05	0.01	0.02	0.00	0.00	1.19	0.05	0.07	0.00	0.01
47	4	26544.9	0.01	0.06	0.00	0.00	0.01	1.10	0.08	0.07	0.00	0.01
48	4	23590.5	0.01	0.00	0.01	0.00	0.00	0.04	0.02	0.02	0.00	0.00
49	3	6197.0	0.00	0.02	0.00	0.00	0.01	1.70	0.07	0.06	0.00	0.00
50	3	6084.0	0.00	0.01	0.00	0.00	0.00	1.33	0.06	0.08	0.00	0.00
51	5	33771.6	0.68	0.00	0.00	0.00	0.00	0.81	0.03	0.02	0.00	0.00
52	3	15487.9	0.01	0.09	0.03	0.00	0.01	5.57	0.19	0.21	0.00	0.00
53	8	76846.7	0.01	0.03	0.01	0.00	0.04	1.86	0.05	0.06	0.05	0.00
54	4	31842.9	0.26	0.00	0.00	0.00	0.00	0.07	0.05	0.04	0.00	0.00
55	3	17051.6	0.17	0.03	0.00	0.00	0.00	0.01	0.13	0.12	0.00	0.00
56	3	49390.6	0.08	0.13	0.05	0.00	0.00	3.26	0.13	0.16	0.00	0.00
Mean	5.6	32708.9	0.07	0.04	0.01	0.01	0.01	1.45	0.06	0.07	0.00	0.00

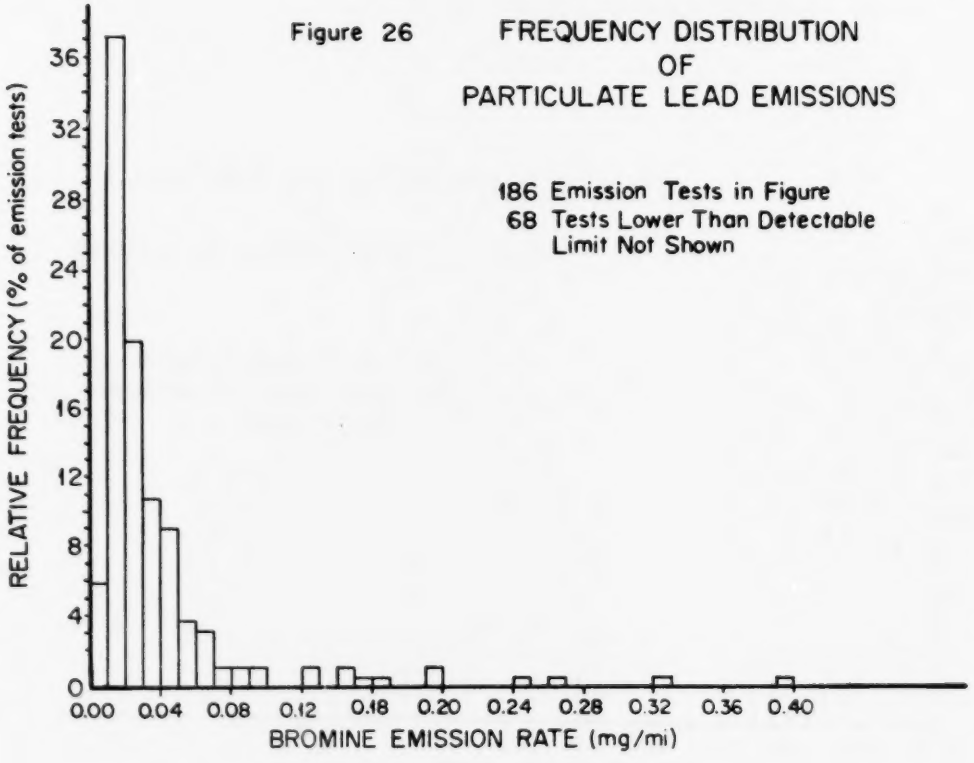
All µg/mi except S which is mg/mi.

Figure 25 FREQUENCY DISTRIBUTION OF PARTICULATE BROMINE EMISSIONS



134 Emission Tests in Figure
120 Tests Lower Than Detectable Limit Not Shown

Figure 26 FREQUENCY DISTRIBUTION OF PARTICULATE LEAD EMISSIONS



186 Emission Tests in Figure
68 Tests Lower Than Detectable Limit Not Shown

Figure 27 FREQUENCY DISTRIBUTION OF PARTICULATE ZINC EMISSIONS

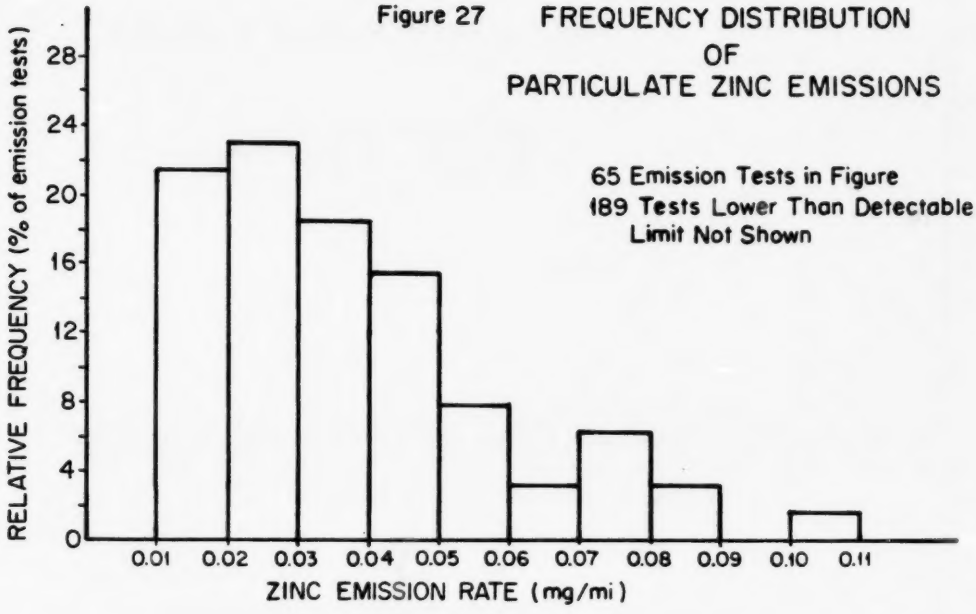
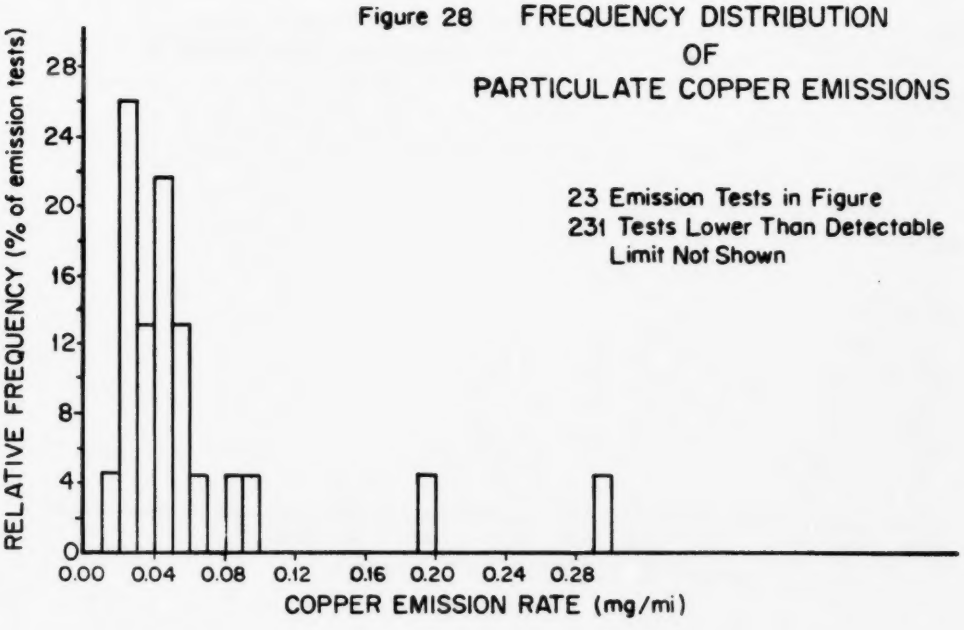


Figure 28 FREQUENCY DISTRIBUTION OF PARTICULATE COPPER EMISSIONS



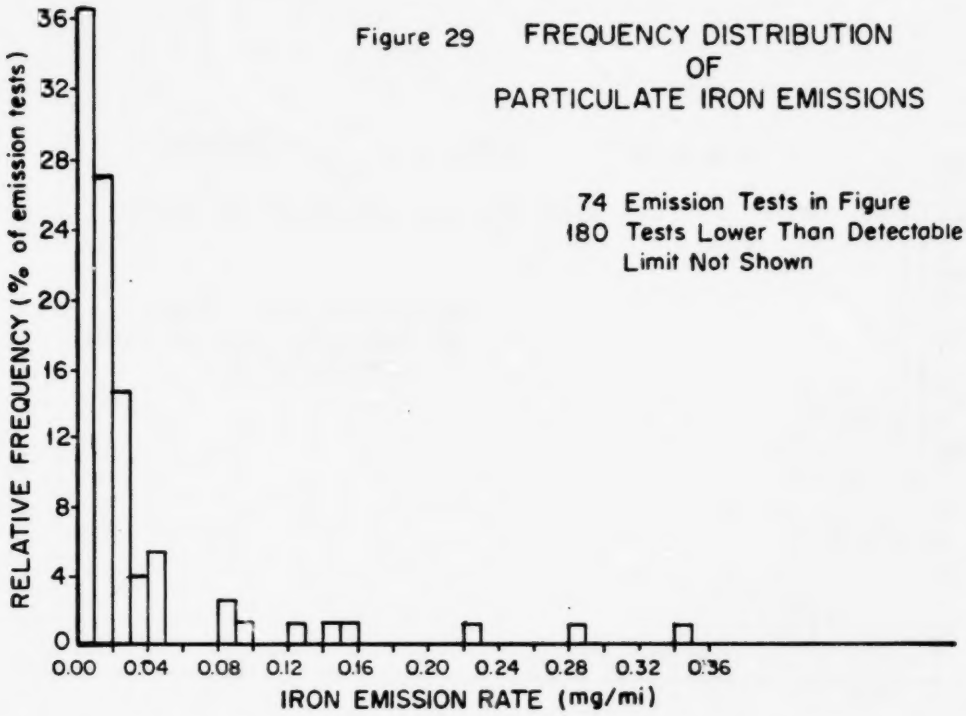


Figure 29 FREQUENCY DISTRIBUTION OF PARTICULATE IRON EMISSIONS

74 Emission Tests in Figure
180 Tests Lower Than Detectable Limit Not Shown

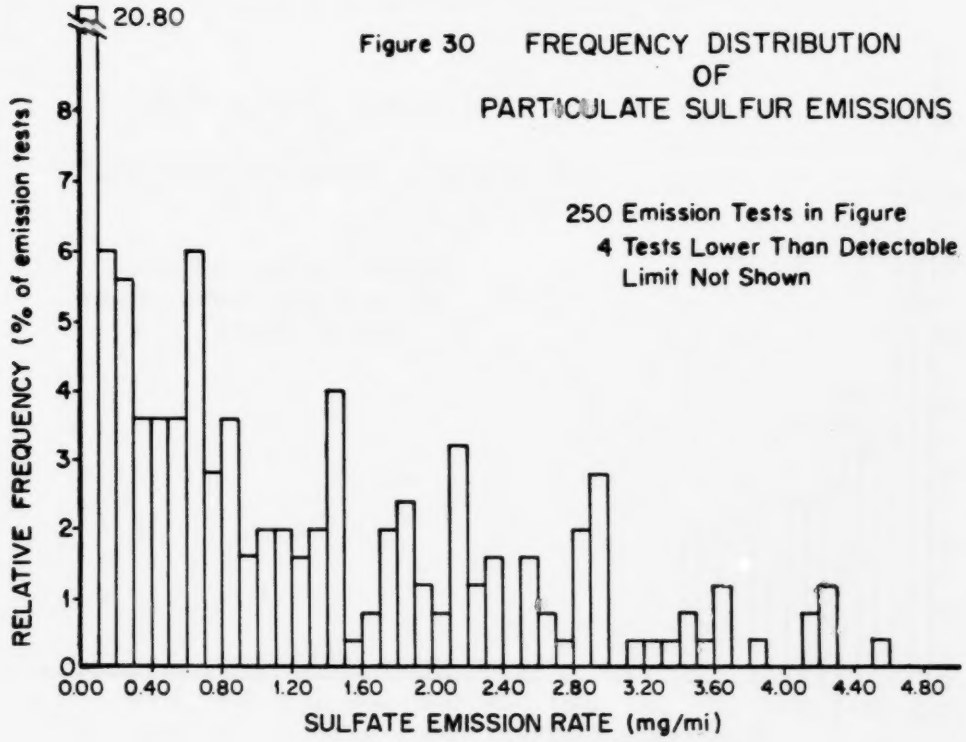


Figure 30 FREQUENCY DISTRIBUTION OF PARTICULATE SULFUR EMISSIONS

250 Emission Tests in Figure
4 Tests Lower Than Detectable Limit Not Shown

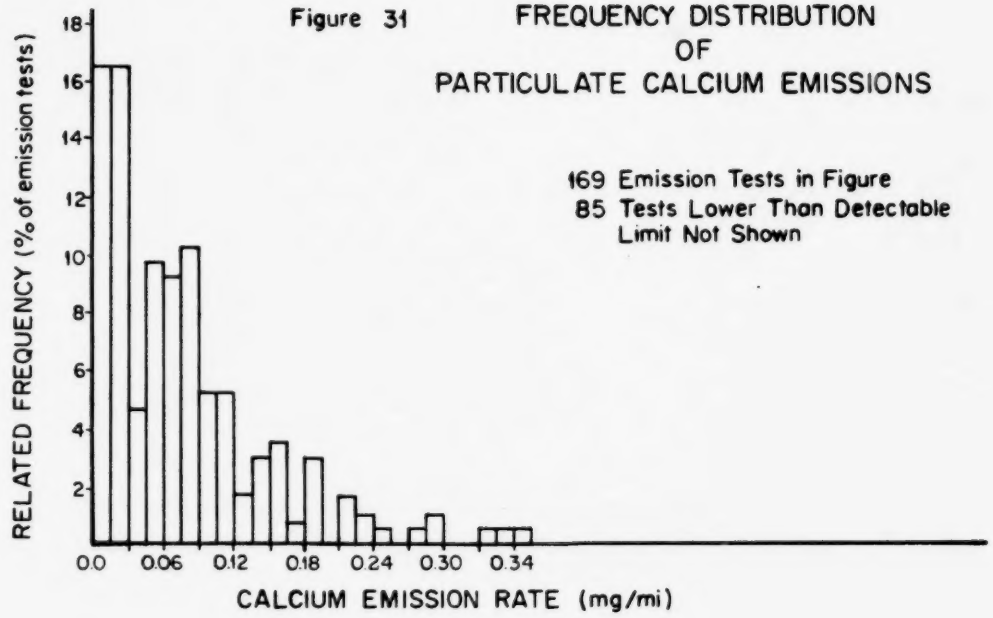


Figure 31 FREQUENCY DISTRIBUTION OF PARTICULATE CALCIUM EMISSIONS

169 Emission Tests in Figure
85 Tests Lower Than Detectable Limit Not Shown

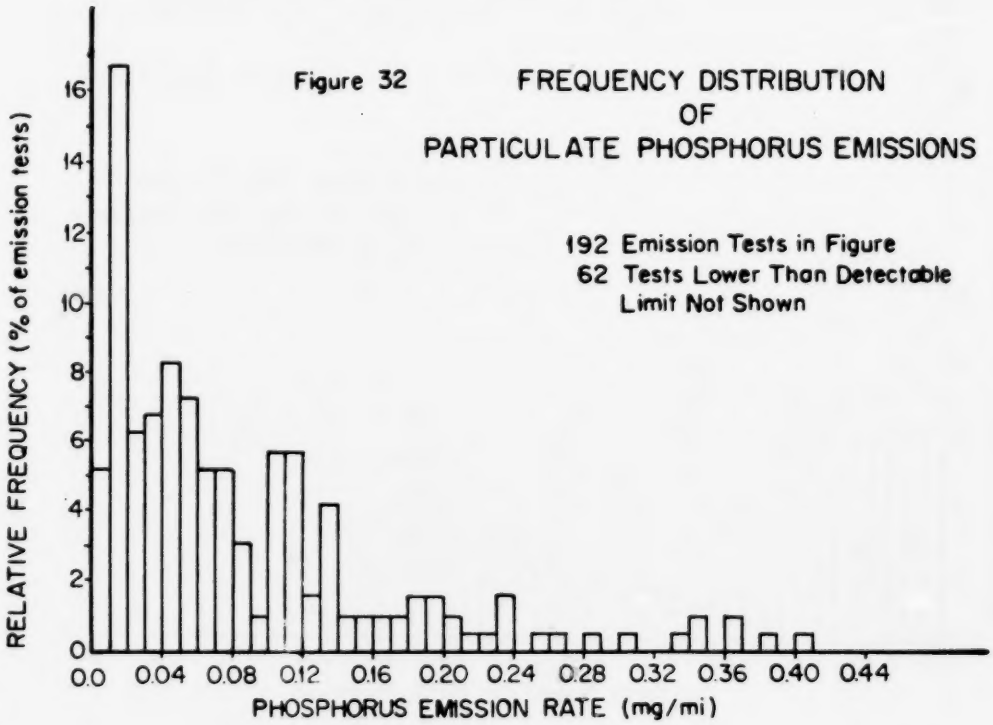


Figure 32 FREQUENCY DISTRIBUTION OF PARTICULATE PHOSPHORUS EMISSIONS

192 Emission Tests in Figure
62 Tests Lower Than Detectable Limit Not Shown

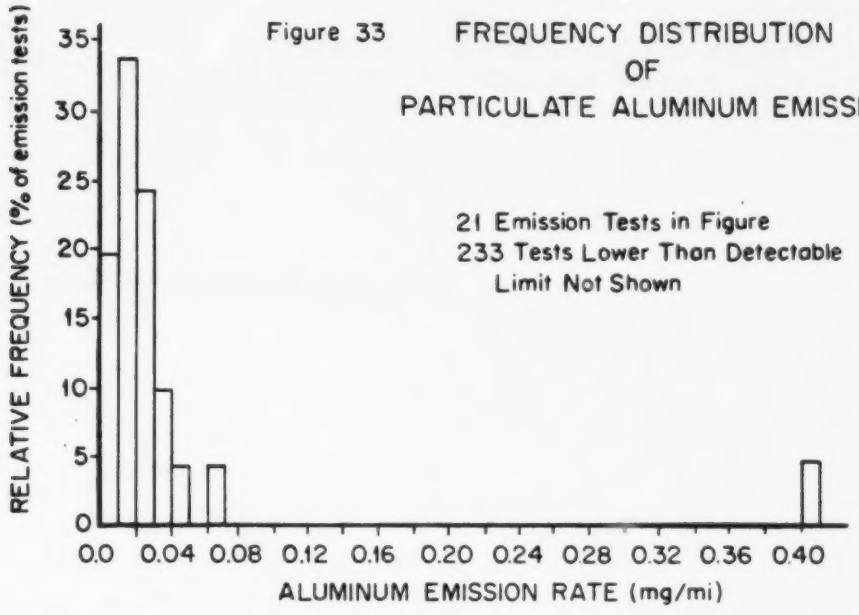


Figure 33 FREQUENCY DISTRIBUTION OF PARTICULATE ALUMINUM EMISSIONS

21 Emission Tests in Figure
233 Tests Lower Than Detectable Limit Not Shown

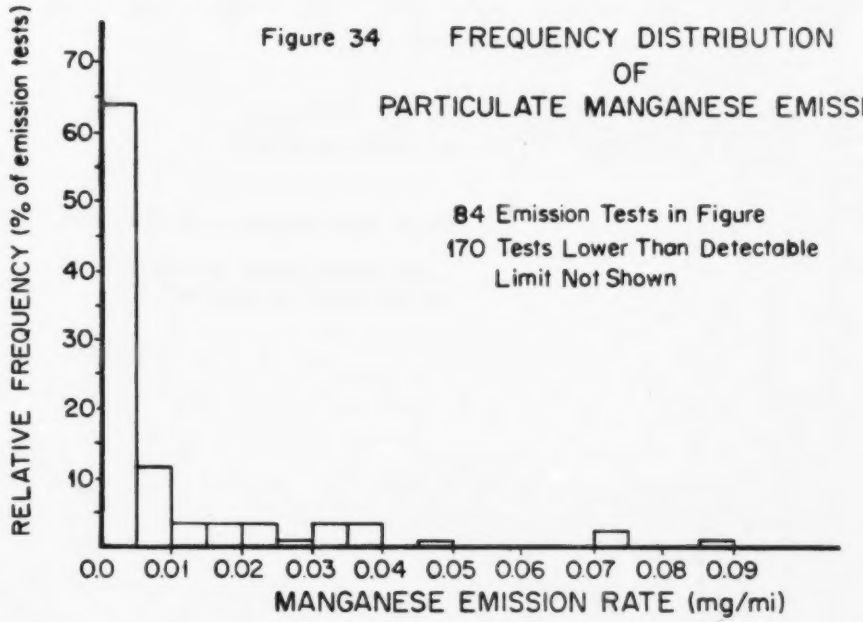


Figure 34 FREQUENCY DISTRIBUTION OF PARTICULATE MANGANESE EMISSIONS

84 Emission Tests in Figure
170 Tests Lower Than Detectable Limit Not Shown

Figure 35

FREQUENCY DISTRIBUTION OF PERCENT
FUEL SULFUR RECOVERY IN PARTICULATE

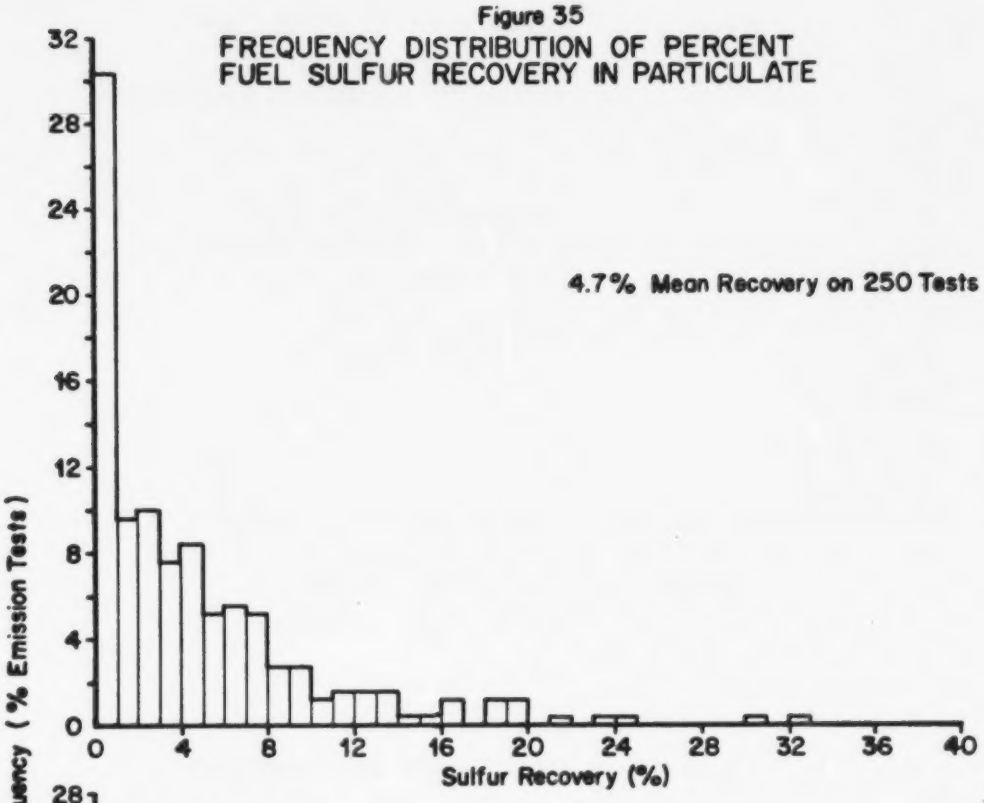
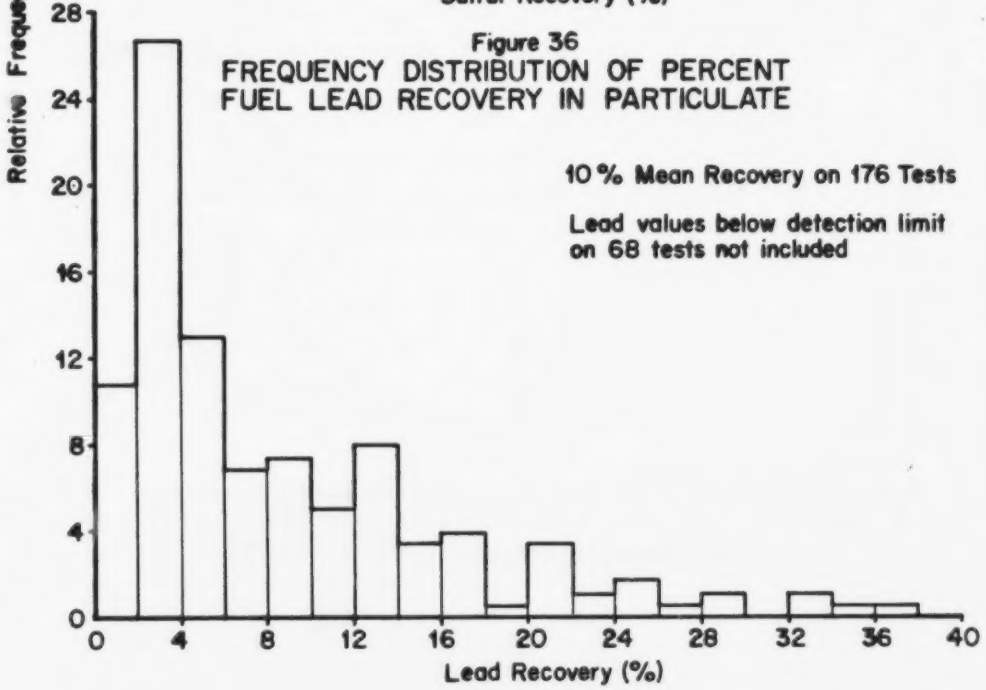


Figure 36

FREQUENCY DISTRIBUTION OF PERCENT
FUEL LEAD RECOVERY IN PARTICULATE



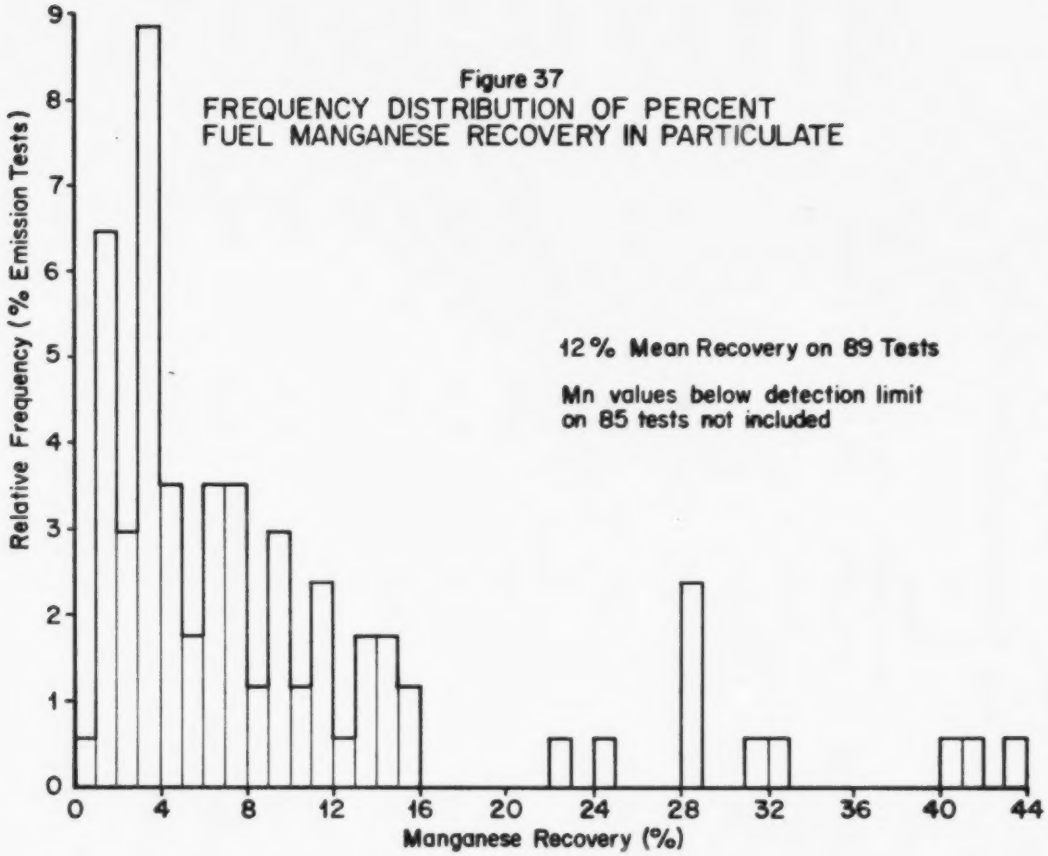


Figure 37
FREQUENCY DISTRIBUTION OF PERCENT
FUEL MANGANESE RECOVERY IN PARTICULATE
12% Mean Recovery on 89 Tests
Mn values below detection limit
on 85 tests not included
Relative Frequency (% Emission Tests)
0
1
2
3
4
5
6
7
8
9
0
4
8
12
16
20
24
28
32
36
40
44
Manganese Recovery (%)

Table 17

Total Particulate Subclassification

Classification	# of Tests	Total Particulate (mg/mi)	Sulfate (mg/mi)	Σxrf non-sulfur (mg/mi)	ΣIC non-sulfur (mg/mi)	% of Total Particulate (Sulfate+xrf+IC)
All Tests	214	6.86	4.44	0.25	0.14	64.38
Ford Tests	29	11.13	7.99	0.21	0.08	69.30
GM Tests	82	4.15	2.10	0.29	0.19	58.26
Chrysler Tests	103	7.81	5.31	0.23	0.12	67.88
Total Particulate:						
< 3 mg/mi	72	1.61	0.67	0.14	0.11	57.48
< 10 mg/mi	163	3.87	2.19	0.23	0.15	62.56
> 10 mg/mi	51	16.41	11.62	0.31	0.13	70.21
Tests in Mileage Interval:						
0-10 k mi	46	7.65	5.92	0.26	0.17	73.39
10 k - 35 k mi	127	6.76	4.15	0.22	0.14	62.30
> 35 k mi	41	6.25	3.68	0.33	0.10	60.75

SECTION 6

CATALYST ACTIVITY TESTS

INTRODUCTION

Near the completion of the data collection phase of the project the test protocol was modified to include raw exhaust measurements before and after the catalyst through sample ports welded into the exhaust system. Data were collected at idle, 30 mph and 50 mph cruise. Parameters measured were HC, CO CO_2 concentrations, and exhaust gas temperatures.

Thirteen of the 56 cars had left the project prior to the introduction of catalyst activity testing, leaving 43 cars in the catalyst activity test data base. Results of the before/after catalyst tests are summarized in Tables 18, 19, and 20 for idle, 30 and 50 mph test modes, respectively.

RESULTS AT 30 AND 50 MPH

Conversions of HC and CO for 30 and 50 mph tests were used to identify those cars with active catalysts. Using an arbitrary criteria of 75% HC and 90% CO conversion, 70% of the 43 cars tested were active at the last test in the project. A breakdown by catalyst system configuration gave the following percentage of active catalysts in each group: 1) monolith without air pump, 73%; 2) monolith with air pump, 88%; and 3) beaded without air pump, 54%. Since this activity test was performed as the last test for each car, we conclude that the large majority of tests during the study were performed on cars with active catalysts.

RESULTS AT IDLE

Many of the catalysts identified as active for CO oxidation at 30 and 50 mph were inactive at idle. For example, Table 21 shows a comparison of results for two cars, similar in their 30 and 50 mph activities, but exhibiting markedly different idle CO conversions. For car 23, engine-out idle CO of 1200 ppm is 100% converted, whereas for car 21 no conversion was found with an engine-out idle CO of 15,000 ppm (1.5%). When engine-out CO is high the intrinsic capacity of the catalyst to oxidize CO is overcome by the CO levels present in the gas stream. This phenomena was not apparent for HC conversions at idle.

Table 18 Catalyst Activity Measurements at Steady State: Idle

Car Number	Catalyst Inlet Concentrations(ppm)		Average Converter Temperature(°C)	Catalytic Conversion(%)		Mass Conversion(g/min)		Exhaust Flow Rate SCFM
	HC	CO		HC	CO	HC	CO	
1	1700	1200	347	81	100	0.45	0.80	20.2
4	2300	15800	296	22	0	0.15	0.00	18.6
5	600	700	244	15	0	0.01	0.00	9.2
7	1400	4100	196	22	0	0.04	0.00	8.3
8	9000	35600	216	13	15	0.25	2.21	12.7
9	4500	9000	214	23	89	0.32	5.03	19.1
10	2800	15800	136	4	0	0.00	0.00	5.0
11	1200	14800	218	0	2	0.00	0.09	9.0
12	1400	5300	375	72	99	0.38	3.96	22.9
15	2000	24400	250	23	3	0.12	0.32	15.8
16	900	2700	235	13	0	0.03	0.00	14.2
18	2100	15000	238	33	0	0.17	0.00	14.7
19	3800	13800	417	84	99	1.30	11.27	25.0
20	2800	11200	234	44	17	0.24	0.73	12.0
21	9100	15000	274	86	0	1.30	0.00	10.2
23	1600	1200	295	83	100	0.28	0.51	12.8
25	1500	1400	287	62	100	0.14	0.42	9.0
26	6500	1700	396	89	82	1.52	0.74	16.2
27	1800	10500	260	23	0	0.09	0.00	13.7
28	10000	61200	235	7	1	0.09	0.19	7.7
29	6600	62000	162	34	0	0.21	0.00	5.7
31	7000	1400	360	95	100	1.69	0.71	15.5
32	7800	73500	171	40	23	0.27	2.89	5.3
34	3800	47000	252	27	0	0.29	0.00	17.3
35	1700	8000	303	33	8	0.17	0.40	18.5
36	3600	7600	160	19	0	0.07	0.00	6.7
38	5500	1300	211	43	24	0.46	0.12	11.7
41	4100	36300	144	26	0	0.10	0.00	5.8
42	2000	12500	304	70	85	0.29	4.51	12.9
43	7000	1700	146	11	4	0.09	0.02	7.4
44	1300	3800	298	86	100	0.30	2.05	16.3
45	900	6500	487	67	65	0.24	3.56	25.6
46	3100	26000	350	20	15	0.08	1.14	8.8
47	1800	2700	378	81	100	0.37	1.39	15.6
48	3500	47000	366	27	0	0.12	0.00	7.7
49	4000	4500	136	23	2	0.09	0.02	6.6
50	3300	4400	314	53	35	0.54	0.96	18.7
51	5500	900	290	76	88	0.82	0.31	12.0
52	5500	14000	288	15	8	0.13	0.35	9.7
53	3600	2200	431	79	96	0.57	0.85	12.0
54	8700	2200	294	85	100	1.22	0.74	10.2
55	6800	26500	260	24	12	0.28	1.08	10.6
56	9800	35200	356	0	16	0.00	3.23	17.4

Table 19 Catalyst Activity Measurements at Steady State: 30 mph

Car Number	Catalyst Inlet Concentrations(ppm)		Average Converter Temperature(°C)	Catalytic Conversion(%)		Mass Conversion(g/mile)		Exhaust Flow Rate SCFM
	HC	CO		HC	CO	HC	CO	
1	500	1800	425	87	100	0.28	2.36	39.8
4	1200	1900	366	16	15	0.09	0.28	29.5
5	1200	1100	360	90	100	0.34	0.70	19.4
7	1000	700	330	86	100	0.25	0.44	19.0
8	2300	9200	375	43	34	0.36	2.33	22.7
9	1400	8000	386	82	100	0.41	5.82	22.1
10	1200	1300	352	92	100	0.38	0.90	21.0
11	1100	900	364	84	100	0.34	0.67	22.7
12	1400	1300	380	88	100	0.62	1.33	31.0
15	1300	6500	370	86	99	0.56	6.54	30.8
16	1500	800	343	85	100	0.57	0.72	27.3
18	1400	1300	374	91	100	0.56	1.15	26.7
19	1400	900	392	93	100	0.76	1.06	35.7
20	2000	2600	360	92	100	0.77	2.19	25.6
21	9100	800	382	98	100	2.98	0.54	20.4
23	1400	500	357	91	100	0.48	0.38	23.1
25	1700	19800	462	82	96	0.50	14.21	22.0
26	700	3800	502	76	100	0.30	4.41	35.2
27	1300	3600	465	24	0	0.11	0.00	22.1
28	2400	6000	325	29	0	0.23	0.00	19.9
29	1400	1700	360	90	100	0.32	0.89	15.9
31	1400	400	442	95	100	0.63	0.38	29.0
32	1200	900	310	59	61	0.17	0.27	15.0
34	2500	15500	326	19	0	0.20	0.00	25.7
35	1700	500	362	93	100	0.81	0.51	31.2
36	1400	900	324	80	96	0.37	0.58	20.5
38	1500	800	302	76	87	0.46	0.56	24.4
41	1300	900	354	90	100	0.35	0.55	18.5
42	2200	6500	378	92	100	0.81	5.25	24.5
43	1600	900	340	82	97	0.49	0.65	22.6
44	600	400	422	84	100	0.28	0.49	37.2
45	500	4200	506	67	72	0.23	3.98	40.2
46	3100	19800	424	16	21	0.15	2.53	18.6
47	500	1800	458	82	100	0.26	2.20	37.1
48	2500	6800	425	62	36	0.28	0.90	11.1
49	1300	800	330	89	100	0.41	0.57	21.6
50	1800	4200	450	41	54	0.41	2.54	34.0
51	1300	600	428	91	100	0.70	0.72	36.3
52	1600	3600	428	86	100	0.70	3.18	26.8
53	1000	1400	464	71	99	0.21	0.79	17.2
54	1100	1300	370	88	93	0.36	0.90	22.8
55	5300	50000	394	23	12	0.54	5.46	26.7
56	10000	11900	554	27	44	1.78	7.00	40.7

Table 20 Catalyst Activity Measurements at Steady State: 50 mph

Car Number	Catalyst Inlet Concentrations(ppm)		Average Converter Temperature(°C)	Catalytic Conversion(%)		Mass Conversion(g/mile)		Exhaust Flow Rate SCFM
	HC	CO		HC	CO	HC	CO	
1	100	4800	641	94	100	0.11	11.23	70.9
4	800	900	509	22	39	0.15	0.65	55.7
5	1800	4000	514	85	84	0.87	3.84	34.7
7	700	700	460	94	100	0.48	1.02	44.2
8	600	4400	527	77	99	0.44	8.61	60.0
9	1500	1300	534	82	98	1.05	2.17	51.9
10	900	2200	518	92	100	0.63	3.42	47.2
11	800	1100	526	88	100	0.55	1.63	44.8
12	800	1200	530	75	90	0.74	2.56	72.0
15	500	300	480	87	100	0.43	0.56	56.5
16	800	1500	518	86	99	0.70	2.87	58.9
18	1400	1100	538	91	100	1.21	2.11	58.1
19	900	1200	532	92	100	0.94	2.73	69.0
20	1900	1700	493	94	100	1.03	1.97	35.2
21	8900	1100	512	98	100	5.78	1.47	40.4
23	1300	1000	498	94	100	1.03	1.69	51.2
25	900	2400	492	76	96	0.51	3.62	47.6
26	900	1900	548	95	100	0.96	4.40	70.2
27	600	6000	518	16	0	0.06	0.00	41.9
28	700	1000	494	94	100	0.60	1.74	52.6
29	1100	800	454	94	100	0.49	0.76	29.0
31	600	1500	598	97	100	0.68	3.54	71.7
32	1200	1000	442	90	100	0.51	0.96	29.1
34	700	800	502	94	100	0.61	1.55	58.6
35	1100	1200	501	94	100	0.81	0.51	31.2
36	800	1000	507	86	98	0.45	1.27	39.5
38	1800	200	444	93	100	1.36	0.33	49.6
41	1300	6600	518	94	94	0.67	6.87	33.6
42	1500	1300	516	93	100	1.05	1.98	46.2
43	1300	1200	490	84	97	0.76	1.63	42.6
44	500	800	536	79	99	0.42	1.68	64.5
45	500	900	566	52	64	0.26	1.19	63.2
46	1900	800	593	84	98	0.97	0.96	37.2
47	1000	900	509	84	100	0.81	1.84	62.0
48	1600	2400	587	95	99	0.66	2.09	26.6
49	800	900	473	91	100	0.47	1.21	40.6
50	600	1300	588	94	100	0.60	2.94	68.6
51	600	1300	554	94	100	0.64	2.78	64.8
52	800	1600	536	84	99	0.83	3.78	71.5
53	200	1000	573	87	100	0.09	0.92	29.3
54	600	1400	541	91	100	0.44	2.28	49.3
55	3100	23600	566	34	14	0.89	5.67	51.0
56	9500	29300	628	28	46	3.07	31.89	71.7

TABLE 21

BEFORE/AFTER CATALYST MEASUREMENT COMPARISON

	CAR 21				CAR 23		
	IDLE	30mph	50mph		IDLE	30mph	50mph
Engine out CO (ppm)	15,000	800	1100		1200	500	1000
Average temperature (°C)	274	382	512		295	357	498
Catalyst conversion of CO (%)	0	100	100		100	100	100
Catalyst conversion of HC (%)	86	98	98		83	91	94

ANALYSIS OF CATALYST ACTIVITY RESULTS

Although the steady state test program emphasized a determination of catalyst activity for each car, other catalyst behavior information was obtained. This data has been used to provide an insight into the disparity between idle and high speed CO oxidation, and to provide a possible explanation of SO_2 purge behavior presented in Section 7. Idle catalyst activity corresponds to high-speed activity for cases with low idle CO; however, vehicles with high idle CO exhibit lower CO conversions than can be projected from 30 and 50 mph results, even though sufficient oxygen appears to be present in the exhaust stream during idle. A conservative method was used to project idle catalyst conversions from high speed results. Assuming a first order rate law for CO oxidation on automotive catalysts in the low CO concentration regime (24, 25, 26), rate constants at measured idle gas stream temperatures were calculated by use of the standard Arrhenius law. An activation energy of 30.0 kcal/gmole - ^{o}K was used; this value is consistent with both reported kinetic data (24-29) and apparent activation energies calculated from the present data. Using the above method and a 30 mph rate constant calculated from the data, an idle rate constant was projected. Idle conversions of CO were then calculated from these projected rate constants. Those tests which had measured CO conversions less than the projected conversion were classified as being idle-inactive. Considering only active catalysts (based on 30 and 50 mph conversions), 90% were found to be idle-inactive when idle CO was greater than 1%, but only 21% were idle-inactive for idle CO less than 1%. High CO appears to inhibit CO conversion over catalysts which are active under low CO conditions.

This inhibition of CO oxidation at high CO concentrations (greater than 1%) for catalysts in actual field use agrees with laboratory studies on CO oxidation over supported noble metal catalysts. Kinetic studies (24-27) indicate that CO oxidation is first order in CO below ~100 ppm CO (at approximately one atmosphere reactor pressure), negative order in CO above ~1% CO, but there is a wide disagreement in the 100 ppm to 1% CO range for the temperatures at which automotive catalytic converters operate. Uncertainty in this concentration range partially involves the transition from first to negative order kinetics, but above kinetic studies of this reaction system explain this uncertainty to be a result of the existence of multiple steady states. Various researchers (30-32) attribute this multiplicity to intraparticle diffusion effects, although recent experimental work (26, 33) points to surface-phenomena-based explanations for the multiple steady state (or hysteresis) behavior.

The cited experimental evidence indicates that CO oxidation over noble metals is first order in carbon monoxide at low concentrations. As CO level is increased, a critical CO concentration is reached at which a rapid transition to negative order CO kinetics occurs, accompanied by a large decrease in the oxidation rate. These laboratory results corroborate our field studies where steady-state test segments with high CO concentrations exhibit very poor carbon monoxide conversion, even though the oxygen content of the exhaust

stream (> 2% O_2) favors more complete CO conversions in the catalytic converter.

It appears that the high CO levels found at idle in improperly tuned cars doubly impairs the operation of automotive catalyst systems. Not only do these high idle CO levels place a large load on the catalytic converters in terms of pollutant mass input, but the existence of these high CO levels forces converter performance into a regime characterized by inefficient operation relative to original design specifications.

SECTION 7

SULFUR DIOXIDE EMISSIONS

INTRODUCTION

Most sulfur present in gasoline is emitted from the engine as SO_2. As exhaust gases pass over the catalyst some of this SO_2 may be oxidized to SO_3 which will quickly combine with water vapor in the exhaust to form sulfate aerosol particulate upon cooling. Other sulfur compounds may form in catalysts (34, 36) (e.g. H_2S, COS) and though these, if formed, could have important consequences, they probably do not constitute a significant percentage of the total fuel sulfur throughput. SO_2 in the exhaust can also interact with the catalyst resulting in storage and/or release of sulfur compounds, again principally as SO_2. Thus, measurement of SO_2, though not a complete analysis of sulfur compounds or the primary focus of the study, can provide insight to the dynamic catalyst behavior during various vehicle test modes.

SO_2 was monitored continuously in dilute exhaust. SO_2 mass emitted during any particular test segment was obtained by integration of SO_2 concentration and the known CVS flow. Separate SO_2 mass emission values were obtained for the 5 minute idle periods and the actual test segments. Details of this detection system are given in Section 8.

SO_2 PURGE AT IDLE

Two distinct SO_2 emission patterns were found in the 5 minute idle periods separating the various test modes. The first pattern is characterized by insignificant SO_2 emission in idle periods, consistent with low fuel consumption and correspondingly low sulfur throughput. SO_2 emission dropped monotonically to these idle values when the vehicle was decelerated from either the 50 mph cruise or CFDS.

The second SO_2 emission pattern is characterized by a significant release of SO_2 during the deceleration to the five-minute idle period following completion of the 50 mph cruise or CFDS. Based on fuel sulfur throughput during idle, this quantity of SO_2 can only represent the release of previously stored sulfur from the catalyst. This SO_2 purge is characterized by a maximum emission level up to twenty-five times the stabilized SO_2 level attained during 50 mph cruise. Representative purges in the idle following a CFDS cycle usually exhibit maximum SO_2 emission rates of less than one-half those associated with the 50 mph cruise, and are found to begin during the final idle of the CFDS. Within a given test, there is a reasonable consistency of purge magnitudes for all CFDS cycles. A correlation was found between the magnitude of SO_2 purge and idle CO levels. For example, for all three tests

through 12,753 miles, Car 3 exhibits SO_2 emission behavior similar to the SO_2 trace from Test 41 in Figure 38. Very little SO_2 release is observed during idle periods from this vehicle, characterized by low idle CO. At Test 57 at 20,000 miles this car showed high idle CO and a dramatic change in SO_2 emissions pattern occurred, also shown in Figure 38. Large SO_2 purges are noted during idle periods for this vehicle exhibiting high idle CO.

One percent idle CO is an approximate cutoff value separating small and large idle SO_2 purges. In order to quantify purge phenomena, SO_2 concentrations in the dilute exhaust were integrated during each driving cycle and idle period, yielding corresponding SO_2 mass values for each segment. A ratio of these masses was defined as follows:

$$SO_2 \text{ purge fraction} = \frac{\text{idle purge } SO_2 \text{ mass}}{\text{previous cycle } SO_2 \text{ mass} + \text{idle purge } SO_2 \text{ mass}}$$

Vehicles with idle CO values greater than 1% yield larger purge fractions than those with lower CO values, as illustrated by Figures 39 and 40 for post-50 mph cruise and post-CFDS cycles, respectively.

TOTAL SULFUR RECOVERY

Total sulfur recoveries for a given cycle were calculated as the sum of sulfur output in the form of cycle sulfate and SO_2, as compared to sulfur input computed from fuel analysis multiplied by fuel consumption for the cycle. In general, total sulfur recoveries were considerably less than fuel sulfur input, averaging 32% for all 50 mph cruise tests. When idle purge SO_2 was included, an average of 45% of fuel sulfur was recovered. Corresponding values for the CFDS were 58% and 77%, respectively. Several factors have been considered in an attempt to resolve the difference between fuel sulfur input and measured sulfur species output, but no single satisfactory explanation has been found. Although it is unlikely on the basis of investigation, the most simple explanation would be a systematic error in the SO_2 detection system. More likely are the complexities of long-term sulfur storage and release of different sulfur compounds in relation to the specific driving cycles of the laboratory test, and over-the-road use. In either case, purge fraction is essentially unaffected, being only a relative measure of when SO_2 emission occurs in the test driving cycle.

The magnitude of the idle purge in relation to fuel sulfur input is demonstrated in Table 22 where the ratio of idle period purge SO_2 to fuel sulfur input to the catalyst in the preceding cycle is tabulated as "SO_2 purge sulfur recovery (%)". Marked differences are apparent in purge magnitude for tests with idle CO less than and greater than 1%. Total fuel sulfur recoveries are also listed in Table 22. These "total cycle sulfur recoveries (%)" include the SO_2 purge contribution from the idle following each cycle.

A few vehicles exhibit high CO emissions during the 50 mph cruise (Table 3). Compared to similar vehicles with low CO emissions in the 50 mph cruise, these high CO emitters exhibit lower idle SO_2 purges even though both are

Figure 38

PURGE OF SO_2 FROM CATALYST

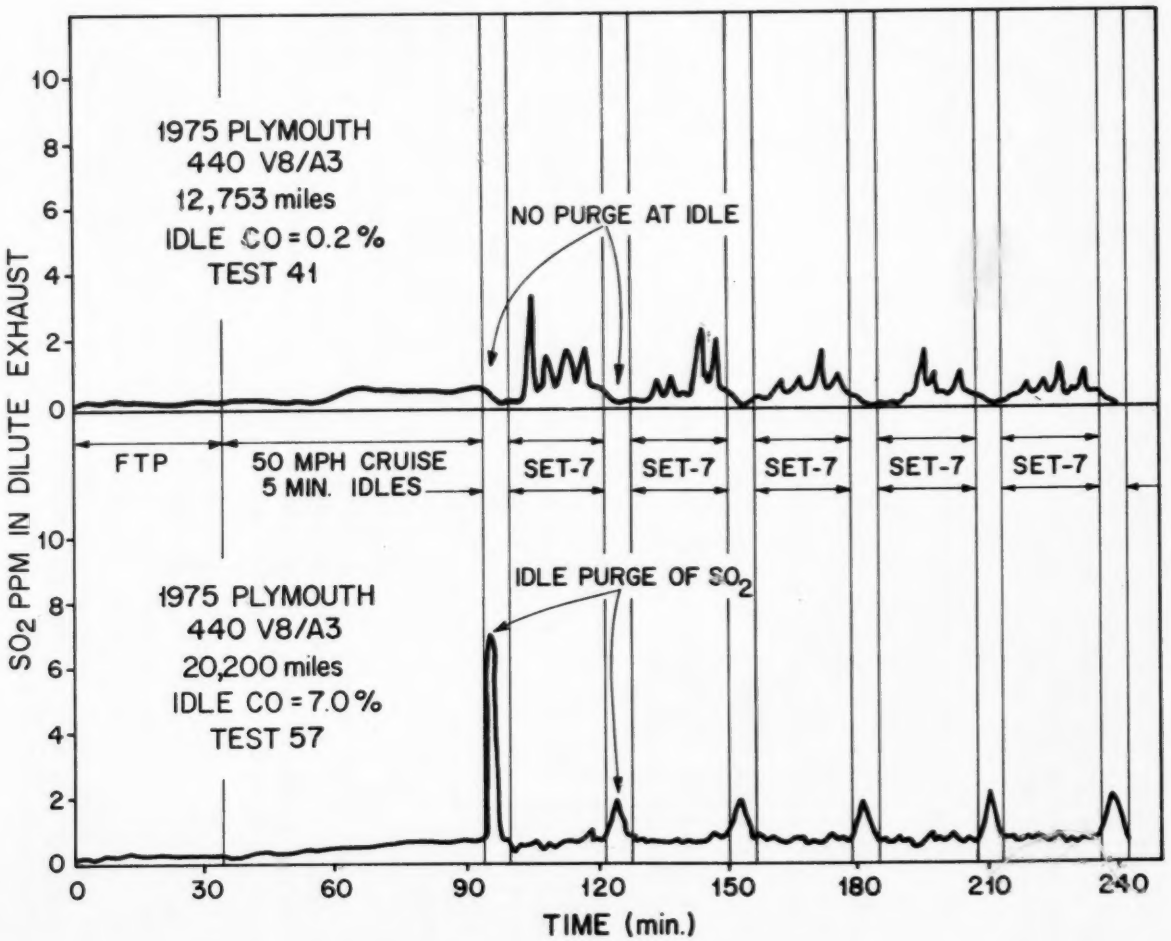


Figure 39

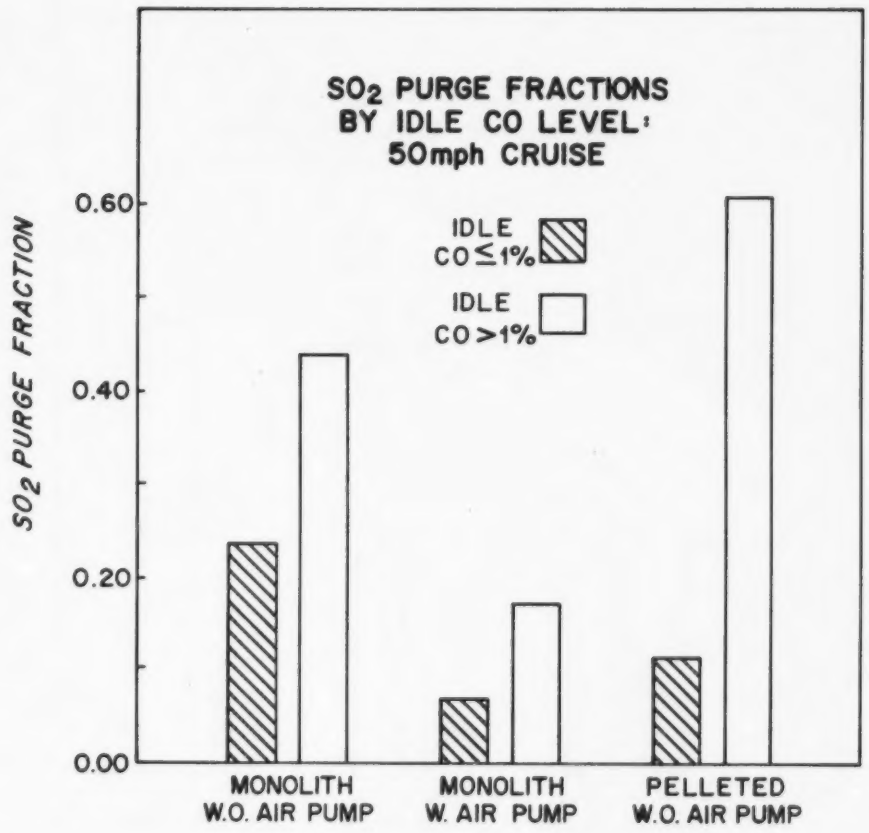

SO_2 PURGE FRACTIONS
BY IDLE CO LEVEL:
50mph CRUISE
IDLE
CO≤1%
IDLE
CO>1%
SO_2 PURGE FRACTION
0.60
0.40
0.20
0.00
MONOLITH
W.O. AIR PUMP
MONOLITH
W. AIR PUMP
PELLETED
W.O. AIR PUMP

Figure 40

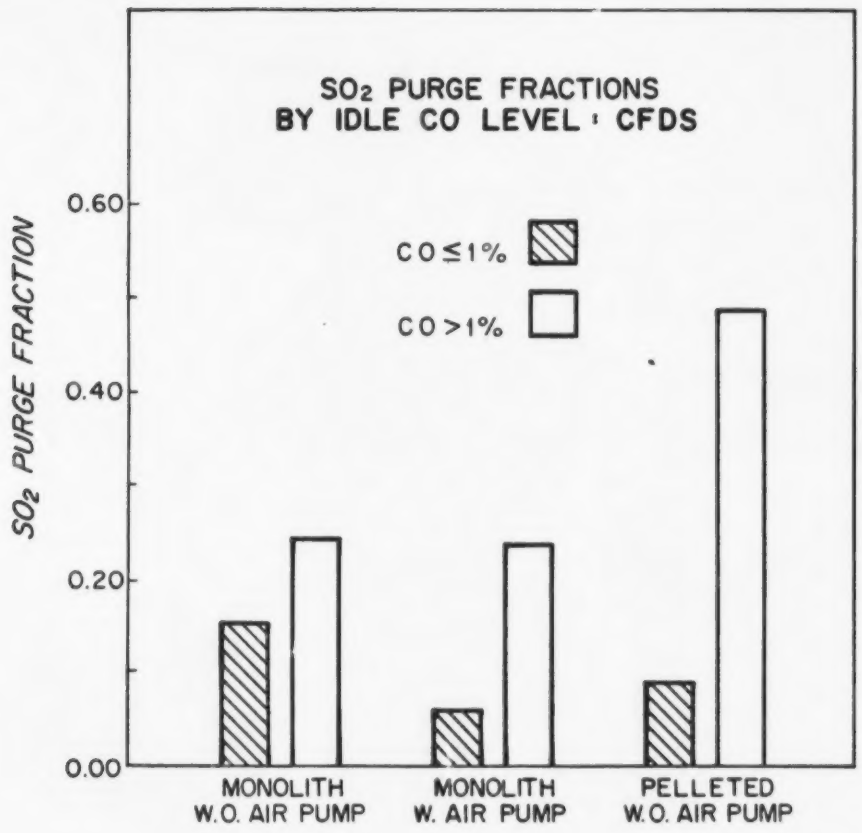

SO2 PURGE FRACTIONS
BY IDLE CO LEVEL : CFDS
SO2 PURGE FRACTION
0.60
0.40
0.20
0.00
CO≤1%
CO>1%
MONOLITH
W.O. AIR PUMP
MONOLITH
W. AIR PUMP
PELLETED
W.O. AIR PUMP

Table 22

Fuel Sulfur Recovery

Category	SO_2 Purge Fraction		SO_2 Purge Sulfur Recovery(%)		Total Cycle Sulfur Recovery(%)	
	50mph Cruise	CFDS Cycle	50mph Cruise	CFDS Cycle	50mph Cruise	CFDS Cycle
A) Monolith Without Air Pump (111 tests)						
All Tests	0.39	0.22	15.3	16.5	45.2	77.2
CO < 1%	0.24	0.16	8.0	11.8	41.8	76.1
CO ≥ 1%	0.44	0.25	17.8	18.2	46.5	77.6
B) Monolith With Air Pump (37 tests)						
All Tests	0.11	0.13	5.3	9.2	57.2	76.8
CO < 1%	0.07	0.06	2.0	3.6	49.7	76.7
CO ≥ 1%	0.17	0.24	10.1	17.3	68.2	77.0
C) Beaded Without Air Pump (72 tests)						
All Tests	0.39	0.29	13.6	20.6	33.8	67.1
CO < 1%	0.12	0.09	2.4	5.7	22.8	64.2
CO ≥ 1%	0.62	0.49	24.8	35.5	44.7	70.1

characterized by idle CO in excess of 1%. Finally, a comparison of tests performed at low mileage (< 15,000 miles) and high mileage indicates no statistically significant effect of mileage accumulation on SO_2 purge behavior.

DISCUSSION OF SO_2 PURGE PHENOMENA

Comparison of occurrences of SO_2 purges during idle periods characterized by high CO levels provides a basis for relating SO_2 purges and catalyst operation. With this connection taken into consideration, analysis of catalyst operation under high CO level conditions points to two plausible hypotheses for the existence of SO_2 purges.

Parametric temperature sensitivity of the reactor system to relatively small changes in converter inlet conditions (i.e. CO concentration) may explain these SO_2 purge patterns. However, temperature data obtained since our earlier analysis(11) of this SO_2 release mode indicate that catalyst temperature excursions do not appear to be sufficient in most cases to account for release of significant SO_2 during idle periods. Even though CO loads on the catalyst systems are sufficiently high, the very low conversions characteristic of the negative order CO kinetic regime do not result in heat production rates large enough to yield significant temperature increases within in catalyst substrate.

An alternative explanation of the occurrence of SO_2 purges focuses upon surface phenomena characteristic of supported noble metal catalysts operating in the presence of high levels of carbon monoxide. CO oxidation at these conditions appears to be negative order in CO because of the strong adsorption of CO on platinum relative to other species present in the engine exhaust stream(24, 25, 26). As gas phase CO concentrations increase, surface coverage by adsorbed CO (on Pt) increases to the point where adsorbed O_2 (necessary for the oxidation reaction) is displaced by adsorbed CO, thereby reducing the CO oxidation rate. Our evaluation of the pertinent Langmuir-Hinshelwood type rate equations for CO oxidation indicates that the surface coverage of adsorbed oxygen in the catalyst falls off faster than the corresponding rise in CO surface coverage with increased gas phase CO levels. Therefore, since the CO oxidation rate is proportional to a product of O_2 and CO surface coverages, the overall CO oxidation rate falls off with increasing CO gas phase concentration at high CO levels. If high CO levels strip the catalytic surface of adsorbed O_2, the same phenomena can occur with adsorbed SO_2 and other sulfur-bearing species.

The following scenario is proposed to explain the purge of SO_2 after deceleration to idle in the presence of high idle CO levels. The large increase in gas phase CO concentration coincides with deceleration to idle results in a much greater concentration of CO on the catalyst surface than characteristic of non idle operation during the previous test cycle. Catalyst surface coverage by CO becomes so large that significant amounts of adsorbed O_2, SO_2 and possibly other sulfur-bearing species are quickly stripped off the catalytic surface and dumped into the converter gas stream, creating an SO_2 purge. This surface phenomena model of SO_2 purges is supported by the finding that purge magnitude correlates with idle CO concentration.

Also in agreement with the above proposed hypothesis is the observation that no significant SO_2 purges were found for vehicles exhibiting high CO emissions during the 50 mph cruise despite the high idle CO exhibited by these same vehicles. If the exhaust during the 50 mph cruise has high CO levels, then the corresponding large CO surface coverages limit the amount of SO_2 adsorbed during the 50 mph cruise. The advent of high idle CO during the subsequent idle period does not result in a SO_2 purge because very little adsorbed sulfur is available for stripping off into the gas stream during idle.

SECTION 8

EXPERIMENTAL PROCEDURES AND EQUIPMENT

EMISSIONS TESTING

Background

This study was initiated in response to the need for data on sulfate emissions from catalyst cars during extended periods of mileage accumulation in consumer use. Regulated emissions, fuel consumption, non-sulfate particulate, and tune-up parameters were also of interest for cars in the study since 1975 marked the public introduction of oxidative catalyst emission control technology. The testing sequence adopted to obtain these data at each vehicle test point is shown in Table 23. In the course of two and one half years of data collection, modifications were incorporated to this initial test protocol. These changes are listed at the bottom of Table 23 with the vehicle test number at which the change was instituted. Table 24 shows the typical time-of-day schedule for the various test segments.

Vehicle Check-In and Soak

Fuel and Hour Meters --

Upon introduction to the test group, each vehicle was outfitted with an engine hour meter (Engler Instrument Co., Model J12N6) and a totalizing fuel meter (Service Recorder CO., Service Oil Meter). These meters remained on the vehicle throughout the project. A typical fuel meter installation is shown in Figure 41. The fuel meter is a positive displacement type (no minimum flow requirement) with an accuracy of $\pm$ 1%. Fuel meters and a protecting fuel filter were installed between the fuel pump and carburetor. The hour meter was connected to the ignition switch and was in operation whenever that switch was in the "start" or "run" position.

Tank Fuel Sample --

Vehicles were tested in "as received" condition such that owner's tank fuel was used whenever possible. Since the length of each test was approximately 120 miles, the vehicle tank had to be at least 1/2 full prior to testing. When vehicles were delivered to AEL with insufficient fuel for the entire test sequence, enough additional commercial lead-free gasoline was added (and recorded) from the AEL fuel facility to perform the test. When sufficient fuel was in the tank, a one gallon sample was pumped, as shown in Figure 42. These fuel samples were shipped in lots of 10 to the EPA Source, Fuels and Molecular Chemistry Section in Research Triangle Park for analysis.

TABLE 23

Data List for Each Emissions Test

Test Segment	Measurements
Vehicle Check-In before 12-20 Hour Soak	Idle HC, CO; Engine Analyzer Check-in (ignition, timing, power balance, EGR, etc.) Visual emission system integrity. Tank fuel sample: Sulfur, Lead, Phosphorous, Manganese, Reid Vapor Pressure, API Gravity, Density, Distillation (Note 1) Odometer, Engine hour meter, totalizing fuel meter.
1975 FTP	Gaseous emissions: HC, CO, NO_x, CO_2, SO_2 One 47mm fluoropore filter for entire FTP: Total particulate mass, Soluble sulfate by Barium Chloranilate (BCA) SO_2 trace in dilute exhaust and mass by continuous integration. O_2 continuous trace in raw exhaust.
1-Hour - 50 MPH Cruise	Same as for FTP with 1 additional 47mm fluoropore filter for Particulate Elemental Analysis by X-ray Fluorescence: Aluminum, Phosphorous, Sulfur, Calcium, Iron, Copper, Bromine, Zinc, Platinum, Lead and Manganese. Anions: Cl^-, Br^-, $PO_4^=$, Fl^-, NO_3^- by IC.
5-Minute Idle Periods	SO_2 trace, mass by continuous integration. Soluble sulfate mass by BCA from 47mm filters collected: A) one filter for first idle after 50 cruise and B) last 3 idle periods averaged on single filter (Note 2)
Five CFDS cycles followed by 5-minute idle periods (Note 3)	Same as for FTP.
HFET (Note)	Same as for FTP.
Three, 15-minute steady state (Idle, 30mph, 50mph) raw exhaust tests (Note 5)	HC, CO, CO_2, O_2 and temperature before and after catalyst during last 10 minutes of each segment.

NOTES:
1) Added manganese analysis from tank fuel after test #149, 12/76.
2) Dropped idle filters after test #162, 3/77.
3) Dropped last three CFDS segments after test #162, 3/77.
4) HFET segment added at test #218, 8/77.
5) Added steady state converter performance segments at test #218, 8/77.

Table 24

Test Day

Typical Time	Test Segment
2:00-4:00	Deliver loan vehicle and pick-up test vehicle.
3:00-5:00	Check-in test vehicle, collect fuel sample, initiate cold soak, weld ports for raw exhaust test, swap tires.
7:00-9:00	Begin FTP testing.
9:00-10:00	Begin one hour 50 mph cruise.
10:00-11:00	Begin CFDS cycles.
11:00-1:30	Begin HFET and before/after catalyst tests.
12:30-2:00	Prepare test vehicle for owner return.
1:00-3:00	Return test vehicle, pick up loan vehicle.

Figure 41. OTR Fuel Meter Installation.

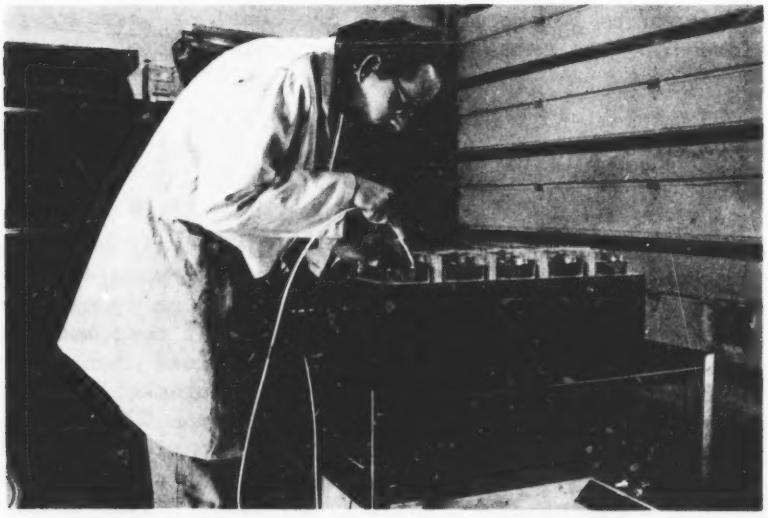


Figure 42. Collection of Tank Fuel Sample.

Photography by Robert Johnson

Analyses performed were: Sulfur, Lead, Phosphorous, Reid Vapor pressure, API gravity, density, and distillation. Analysis for manganese was added in December 1977.

Engine Analyzer --

Figure 43 shows a typical engine check-in progress. Engine and idle emission parameters were recorded on a check-in sheet shown in Figure 44. The engine analyzer was a Sun Model EET940. A Sun "EPA-75M" HC/CO analyzer was used through most of the project, but was replaced by a Horiba Mexa-300 analyzer for the last six months of testing. Both instruments were initially calibrated against NBS traceable gases and checked with working gases periodically thereafter. EGR valve operation was checked by manual application of vacuum to the EGR valve with observation of drops in manifold vacuum and engine idle speed confirming its operation.

Cold Soak Preparation --

After check-in, the vehicle was prepared for cold soak. During winter months front and rear wheels were swapped to avoid testing with snow tires, many of which were studded. The dynamometer tire pressure was set at 35 psi for all tests. The checked-in vehicle was normally placed in cold soak about 4:30 p.m. for testing the next morning. The FTP portion of the test sequence normally began about 9:00 a.m., resulting in 14-16 hours of soak. Vehicles were moved to the test bay from the cold soak bay by a car mover shown in operation in Figure 45. Vehicles were soaked in a climate controlled room with a maximum/minimum temperature thermometer adjacent to the car. Soak temperature control set point was 72°F, with an extreme minimum of 65°F and extreme maximum of 75°F throughout the two and one-half years of testing.

For the final test on all but 13 vehicles, raw exhaust sampling and temperature measurements before and after the catalyst were added. Sample ports were welded into the exhaust system to obtain these data as shown in Figure 46.

Emissions Testing Equipment

Test Bay --

The AEL test bay is shown in Figures 47-49. Two air conditioner/electric heater/humidity control units circulate 15,000 cfm of room air through overhead ducts parallel to the vehicle as positioned on the dynamometer. Temperature control was maintained at 22 $\pm$ 2°C regardless of test mode or seasonal variation; humidity control was less responsive to load changes, and was set at 50% relative humidity with a range of 30-60% RH bracketing all test conditions. The dynamometer used for testing was a Clayton CTE-50-full lift, equipped with automatic road load and direct-drive variable inertia simulation. A Hartzel Model N24-UW fan (5250 cfm) was directed at the front of the vehicle. A 20-inch squirrel cage blower (7000 cfm), Dayton Model 3C011, was directed diagonally from the drivers side of the vehicle toward the rear wheels. This blower is located behind the converter to provide rear-tire

Figure 43. Vehicle Check-In.

Figure 44. Vehicle Check-In Log Sheet

AUTOMOTIVE EMISSIONS LABORATORY (518) 457-3200
New York State Department of Environmental Conservation
50 Wolf Road, Albany, New York 12233

ENGINE ANALYSIS CHECK IN SHEET

TEST NUMBER _____ TEST DATE_____ DATE VEHICLE IN _____

MAKE _____ MODEL_____ YEAR_____

	TEST PROCEDURE	READ	SPECS.	RESULTS	GOOD	BAD
START	Cranking Voltage	Voltmeter				
	Cranking Coil Output	Scope (Display)				
	Cranking Vacuum	Vacuum Gauge				
IDLE	Idle Speed	Tachometer				
	Dwell	Dwell-Meter				
	Initial Timing	Timing Advance Unit				
	Hydrocarbons P.P.M.	Hydrocarbons Meter				
	Carbon Monoxide	Carbon Monoxide Meter				
	PCV Test	Carbon Monoxide Meter				
	Manifold Vacuum	Vacuum Gauge				
CRUISE	Dwell Variation	Dwell Meter				
	Coil Polarity	Scope (Display)				
	Spark Plug Firing Voltage	Scope (Display)				
	Maximum Coil Output	Scope (Display)				
	Secondary Circuit Insulation	Scope (Display)				
	Secondary Circuit Condition	Scope (Raster)				
	Coil and Condenser Condition	Scope (Raster)				
	Breaker Point Condition	Scope (Raster)				
	Cam Lobe Accuracy	Scope (Superimposed)				
	Hydrocarbons P. P.M.	Hydrocarbons Meter				
	Carbon Monoxide Percent	Carbon Monoxide Meter				
	Cylinder Power Balance	Tachometer				
	Record R.P.M.	1 2 3	4	5	6	7 8
ACCEL-ERATION	Spark Plugs Under Load	Scope (Display)				
	Accelerator Pump Action	Carbon Monoxide Meter				
HIGH SPEED	Timing Advance	Timing Advance Unit				
	Charging Voltage	Voltmeter				
	Hydrocarbons P.P.M.	Hydrocarbons Meter				
	Carbon Monoxide Percent	Carbon Monoxide Meter				
	Exhaust Restriction	Vacuum Gauge				

COMMENTS :

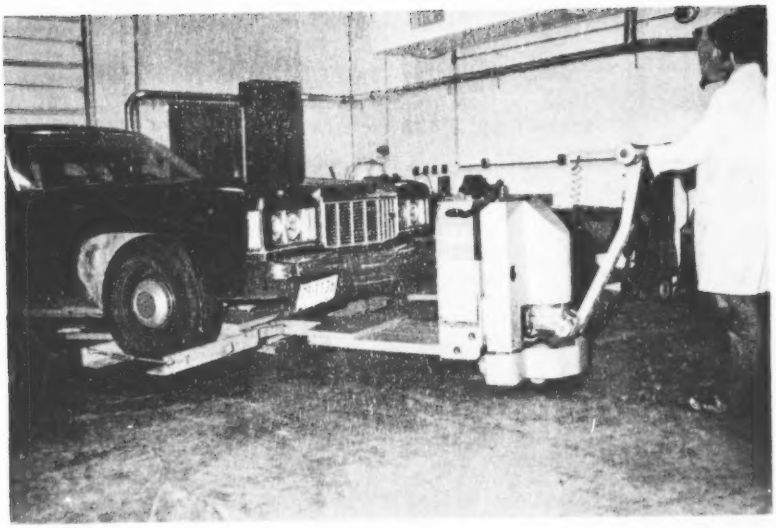


Figure 45. Car Mover Operation.

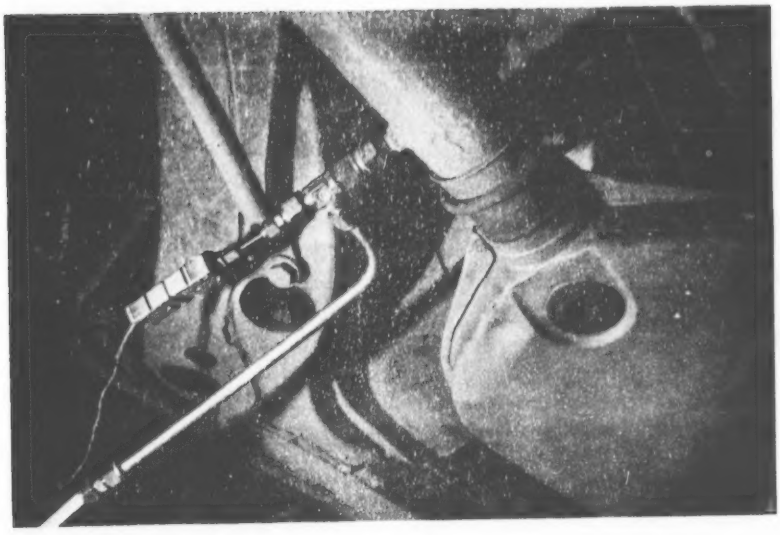


Figure 46. Before/After Catalyst Sample Ports.

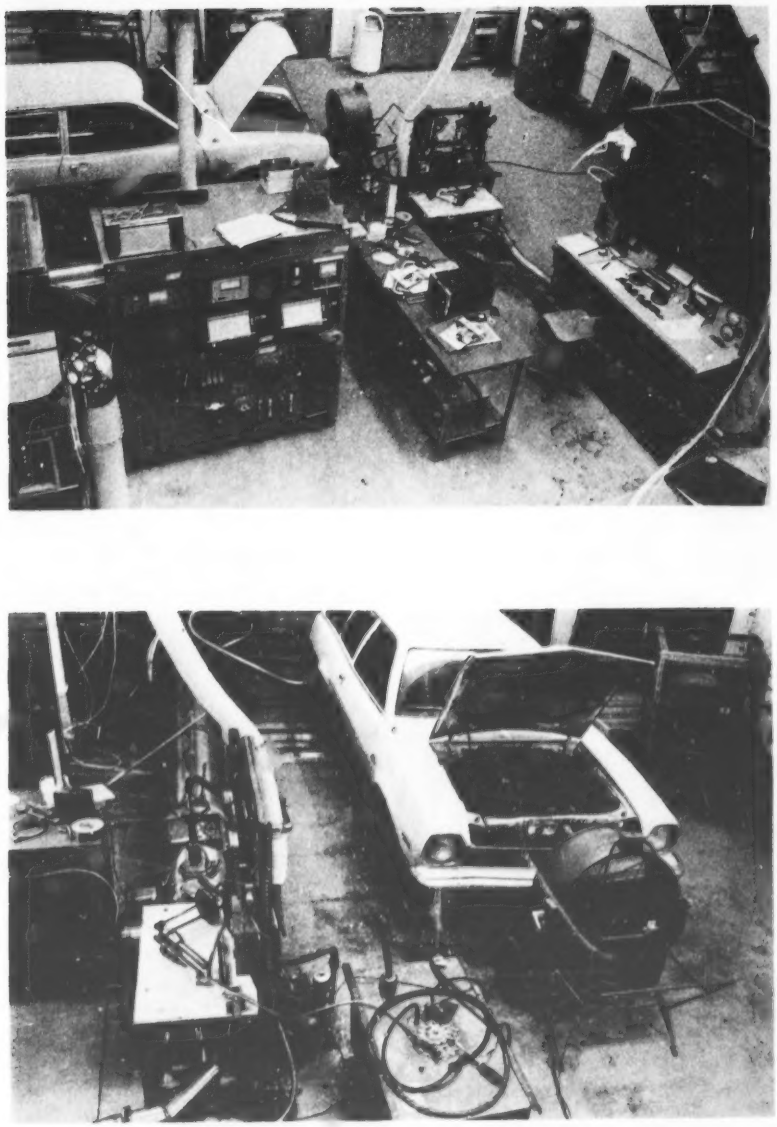


Figure 47. Emissions Test Bay.

Figure 48. Dynamometer, Cooling Fans.

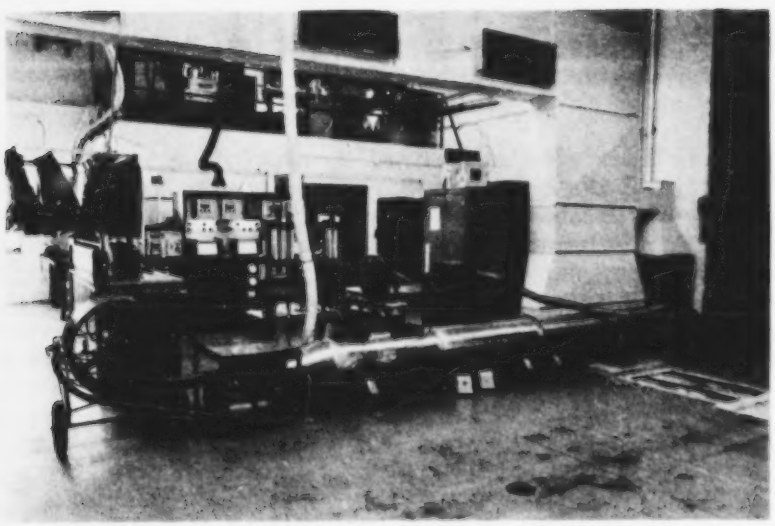


Figure 49. Exhaust Sampling Equipment.

cooling in order to prevent tire failure. These fans are shown in operating position in Figure 48.

Particulate Collection and Exhaust Handling --

Exhaust particulate was collected in a standard dilution tunnel(37, 38) connected between the inlet of the Scott model 302 positive-displacement-pump constant-volume-sampler (CVS) and the vehicle exhaust inlet. CVS flow was a nominal 400 cfm. The dilution tunnel and particulate collection probes are shown schematically in Figure 50. Dilution air inlet to the standard filter box was ducted from the exit of one of the test bay air conditioners. Particulate was collected through two probes (1 in I D x 6 in lengths) into 47 mm Millipore filter holders. These probes and filter holders were rigidly mounted by a quick disconnect clamp to a 6 in diameter probe access port on the dilution tunnel. The probes are shown in Figure 51. Flow control through the probes was regulated by 10-turn Parker-Hannifin (N-800-B11) valves. Flow rate was monitored by Brooks model R-8M-25-2 flow meters. A vacuum gauge between the filter and the control valve was used to make pressure corrections to compute total volume filtered.

The CVS was outfitted with 9 sets of exhaust/background bags to accommodate the test sequence without delays for bag evacuation. Background sample was collected from the dilution air filter box. CVS blower differential and absolute pressures were measured on Merian 10AA25WM-36 and 2QAA25WM manometers, respectively. CVS blower inlet temperature was continuously recorded on a Rustrack Model 2133 thermistor probe strip chart recorder.

Gaseous Analysis --

Bag analysis of HC, CO, CO_2, and NO_x followed the Federal Register sample conditioning and analysis procedures for the 1975 FTP(13). Instruments used for exhaust gas analysis are listed in Table 25.

Oxygen concentration in undiluted exhaust was determined by sampling at the inlet to the dilution tunnel (see Figure 50). The O_2 measurement system is schematically shown in Figure 52.

SO_2 mass emissions were determined by continuous measurement and electronic integration of SO_2 concentration in dilute exhaust, sampled at the dilution tunnel particulate filter station (see Figure 50). The SO_2 measurement system is shown schematically in Figure 53. Output signal from the SM-1000 UV spectrometer was integrated electronically and also strip chart recorded by Disk^{TM} integrator to provide hard copy output of where SO_2 emission occurred in any test segment. Large purges of SO_2 in idle periods were observed in the early tests, and an electronic switching system was designed to restart the continuous electronic integration procedure in synchronization with the CVS bag switches. This switching system, shown in Figure 54, permitted the SO_2 mass to be determined for successive back-to-back test segments.

Emission Test Procedures

Dynamometer --

Dynamometer calibration was established both by recommended Clayton

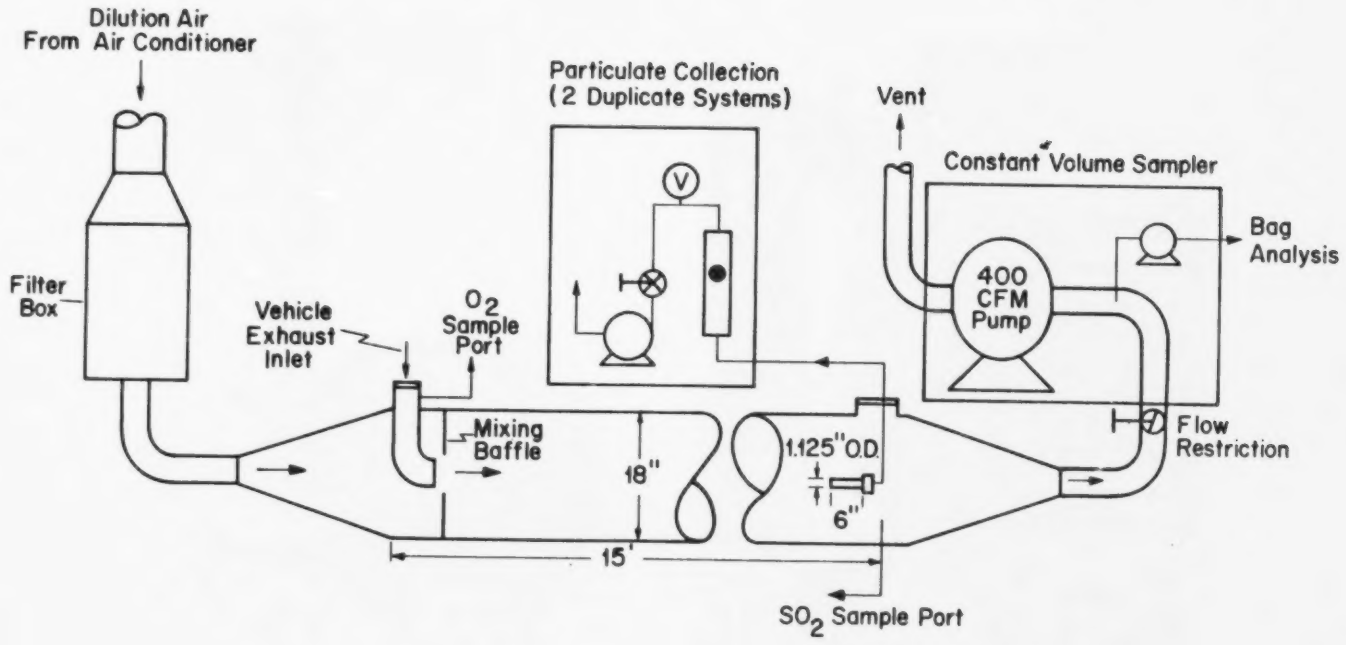
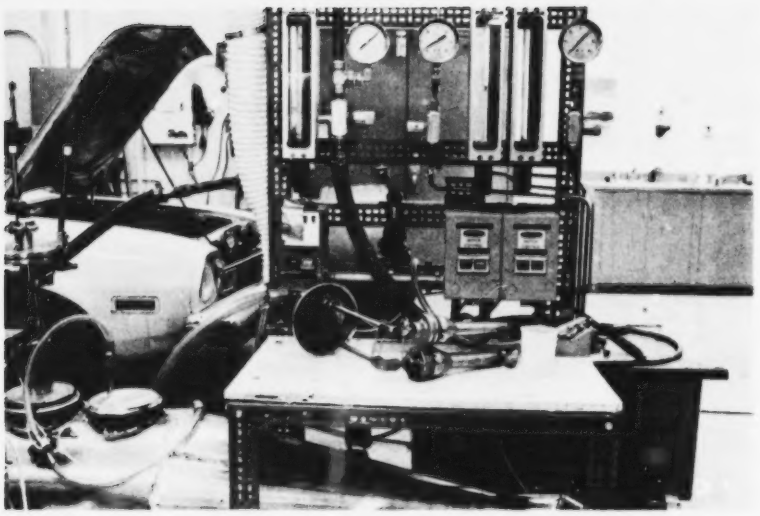


Figure 50. SCHEMATIC OF EXHAUST HANDLING AND PARTICULATE COLLECTION



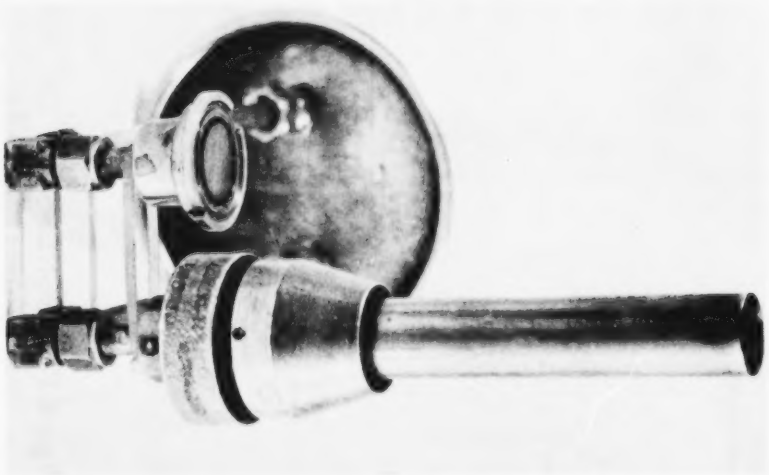


Figure 51. Particulate Sample Probes.

Table 25

Exhaust Gas Measurement Instrumentation

Gas	Manufacturer	Model	Type Instrument	Notes
CO	Ethyl-Intertek	URAS 2T	NDIR	
CO	Horiba	AIA-21-AS	NDIR	Replaced URAS after test #161
CO_2	Ethyl-Intertek	URAS 2T	NDIR	
CO_2	Horiba	AIA-21	NDIR	Replaced URAS after test #249
O_2	Scott	150	Paramagnetic	
HC	Scott	215	FID	
NO_x	Scott	125	Chemiluminescence	
SO_2	Lear-Seigler	SM-1000	2nd derivitive UV Spectrometer	
CO	Beckman	315	NDIR	Used for before/after converter tests
CO_2	Beckman	864	NDIR	
HC	Beckman	400	FID	

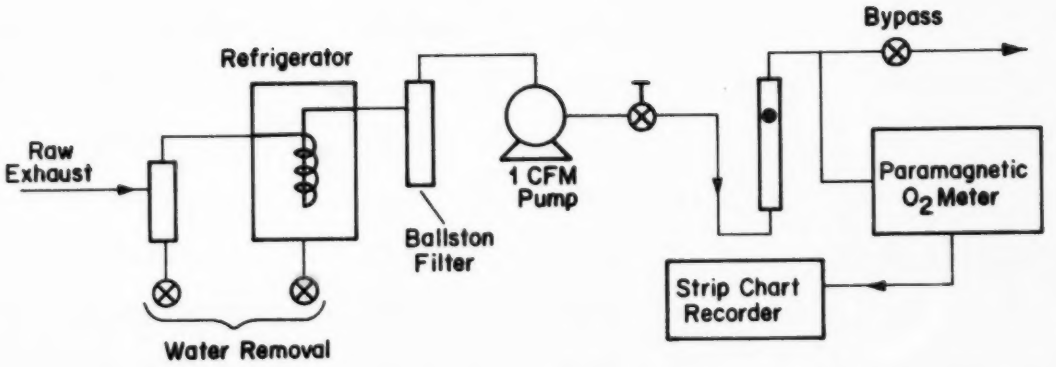


Figure 52. OXYGEN IN RAW EXHAUST SAMPLE SYSTEM

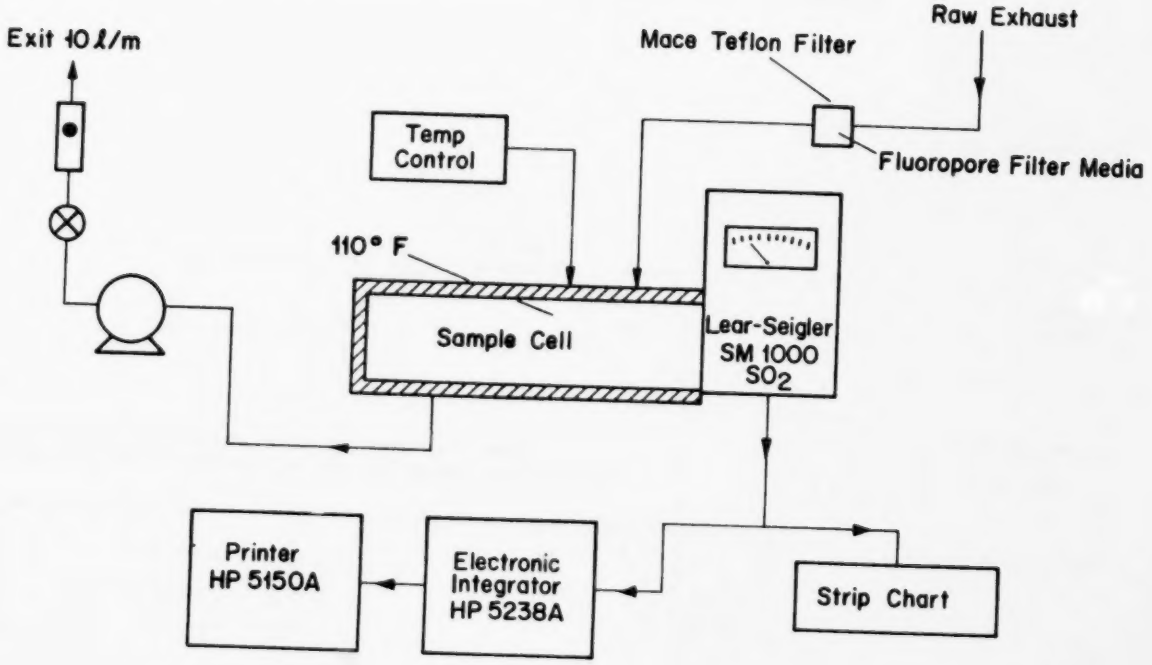


Figure 53. SO_2 MEASUREMENT SYSTEM

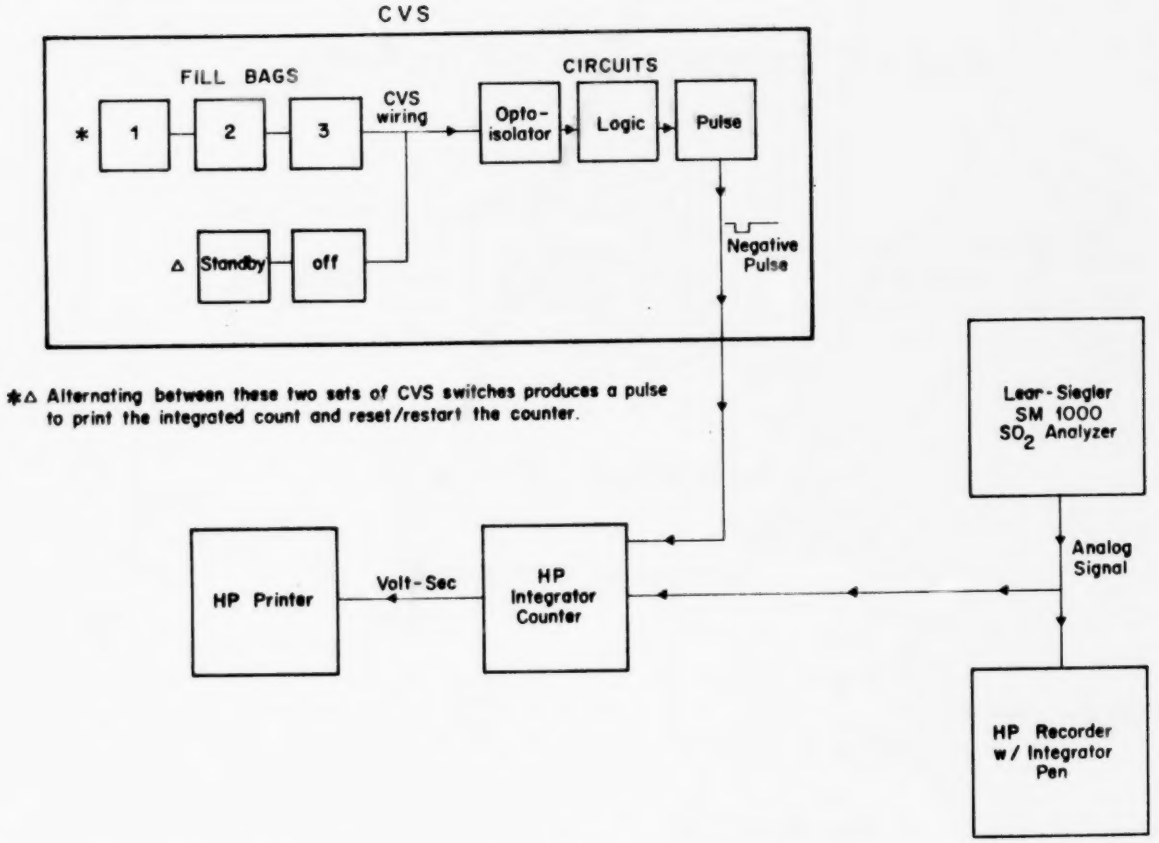


Figure 54. SO_2 ELECTRONIC INTEGRATION SWITCHING SYSTEM

calibration procedures and by coast-down procedures as specified in the Federal Register. Three complete coast-down calibrations were performed in the course of this work. Daily checks on the 50 mph power absorbtion as part of dynamometer warm-up were used to verify stability of calibration. Two drivers aides were used, and these were zero checked and calibrated at 50 mph as part of the daily dynamometer preparation. A Scott Model 201 drivers aide was used for FTP testing, and Varian A-4 drivers aide was used for the CFDS tests. Inertia settings were assigned to test vehicles based on new car certification test data published in the Federal Register (40CFR 3/11/75, 41CFR46 3/8/76).

Particulate Collection --

Hot-wire anemometer measurements were used to measure the flow profile in the dilution tunnel at the particulate sampling station. These experiments verified a flat velocity distribution consistent with fully developed turbulent flow. Mixing of exhaust gas and dilution air was also characterized by injecting propane in the exhaust inlet to the tunnel at a constant rate while performing a traverse of propane concentration across the diameter of tunnel at the particulate sample station. A uniform propane profile was observed indicating satisfactory mixing. The tunnel was swept and washed at 6 month intervals with the debris sent to EPA for analysis. Fluoropore filters, 0.5 micron pore specification, were used for particulate sampling throughout this study. Flow adjustment was frequently required to maintain constant flow as filters became progressively loaded. Vacuum measurements were recorded and used to correct observed flow to standard conditions. A dry gas meter was connected to the exit of this system for several tests in order to confirm the accurate determination of total filter flow.

Constant Volume Sampler --

The Scott Model 302 constant volume sampler (CVS) was extensively flow calibrated using an Autotronics Inc. turbine flow meter (Model 1000 flow computer and Series 100 flow transducer) prior to the beginning of this project. A minute change in calibration was observed for the one additional flow calibration performed during the course of this project to check the system for long-term drift.

Three CVS blower revolution counters were used on an alternating basis as part of the daily propane injection test to check for any deterioration of counter accuracy. Propane injection tests through test #218 were by a gravimetric determination using lecture bottles of propane suspended from an Ohaus balance (Model 71032). Tests beyond #218 used a Horiba critical flow orifice device (CFO model 201). A $\pm$ 5% propane recovery error cutoff was utilized, but this error bound was decreased to $\pm$ 2% without any CVS or instrument calibration changes when the CFO device replaced the cumbersome gravimetric method.

Analytical Instruments --

Instruments for analysis of HC, CO, CO_2, NO_x, and O_2 were calibrated on a monthly basis with laboratory standards. These standard gases were $\pm$ 2% mixtures from the manufacture that were calibrated by the EPA Mobile Sources

Laboratory in Ann Arbor, Michigan. From these primary calibration gases, working span gases were established for daily use. Zero, span, and gain settings were checked as part of the daily preparation before testing, and between test segments. Strip chart recordings were used to determine instrument response and provide a hard copy of all calibration, zero, span, and emission determinations. NO_x converter efficiency was checked as per Federal Register (40CFR Pt. 86) as part of the monthly calibration. Instruments were operated continuously to obtain maximum stability. The URAS-2T CO instrument required the removal of H_2O and CO_2; two banks of Ascarite/Drierite columns were used for all determination on that instrument.

The Lear-Seigler SM-1000 second derivative UV spectrometer was set at 301 nm to detect SO_2 in dilute exhaust. The instrument was supplied with a servo-operated ampule containing SO_2 as a calibration. A series of tests using gravimetric injection of pure SO_2 to the exhaust inlet of the dilution tunnel analogous to a propane injection test confirmed the operation of the system. SO_2 calibration gas was also used directly in the instrument to set the instrument calibration factor. The internal SO_2 span ampule was calibrated from this gas calibration and used for a daily span check. A wet chemical method for SO_2 determination(14) was also used to check for interference from other exhaust species. This method absorbs SO_2 into 3% H_2O_2 as sulfate for subsequent determination by the BCA system used for determination of particulate sulfate. Several vehicle tests with parallel Lear-Seigler and bubbler tests confirmed the instrument calibration and the absence of major interference by other exhaust species.

Laboratory Analysis of Particulate

Filter Handling --

All particulate samples were collected on 47 mm diameter Fluoropore™ 0.5 micron pore size media. Fresh filters from stock were stabilized overnight in a dessicator containing drierite prior to initial weighing. Filters were weighed on a micro-balance housed in a controlled humidity and temperature glove box, shown in Figure 55. Each filter was placed in a numbered petri dish upon weighing and transported to the vehicle test bay in groups of 20 filters. After completion of a test segment filters were immediately returned to the petri dish. The eight filters from each completed test were placed in a dessicator containing dilute NH_4OH vapors for a minimum of 1/2 hour, to stabilize particulate H_2SO_4 as $(NH_4)_2\ SO_4$. The ammoniated filters were then placed in a dessicator containing drierite overnight in order to remove water associated with the particulate H_2SO_4. Since the ammoniation step changes the filter loading according to the amount of H_2SO_4 present, subsequent sulfate analysis results were used to compute the NH_4^+ mass to be subtracted from the total particulate mass to arrive at the mass of water free particulate collected.

Filters were individually placed in 50 ml Poly-cons with 20 ml of 60% isopropyl alcohol to solublize sulfate. The samples were mechanically agitated for one hour prior to filtering the extractate through Whatman #40 filters in preparation for sulfate measurement.

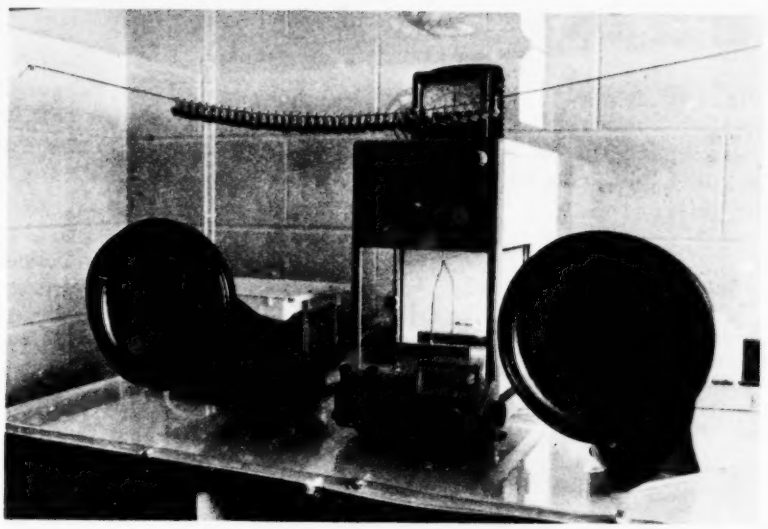


Figure 55. Microbalance for Particulate Mass.

Soluble Sulfate by BCA --

The semi-automated barium chloranilate (BCA) method of Tejada and Sigsby (39) was used for determination of soluble sulfate loadings on the filters. Figure 56 shows the system in operation, while Figure 57 is a schematic of the system. Detection of soluble sulfate occurs by passing liquid sample through a column packed with barium chloranilate; barium sulfate is then formed, releasing chloranilate which is quantitatively detected by a UV detector set at 310 nm. The instrumentation used here was a Technicon Sampler IV and Proportioning Pump III, Valcor 6-port air actuated valve, Instrumentation Specialties Co. high pressure pump, pressure monitor (#1590), flow controller (#314), and absorbance monitor (#UA-5). A Hewlett-Packard 7100B strip chart recorder in parallel with a Columbia Scientific Supergrator II programmable integrator provided necessary output.

Prepared filter extracts were loaded in the Technicon carousel sample holder with several blank solvent and calibration samples of $(NH_4)_2SO_4$. The BCA apparatus was operated on a 6 min cycle, with 4 min to fill the sample loop and 2 min to inject the sample. The BCA column was 1/4 in x 3 in stainless steel, the injection loop 1/16 in x 3 in stainless steel, and high pressure pump rate was 100 ml/min. Integrated peak areas from the calibration standards were used to generate a 2nd order polynomial fit calibration curve for each batch of samples (usually 2 complete car tests). Soluble sulfate values for the samples were computed based on this calibration curve. XRF and Ion Chromatograph analyses of filter samples indicated that interferences of other ions with BCA sulfate determinations were negligible for filters in this study.

Elemental Analyses by XRF --

Elemental analyses of particulate were performed on a Siemens wavelength-dispersive x-ray fluorescence (XRF) spectrometer shown in Figure 58. The basic XRF unit was equipped with a model K-4 x-ray generator and a 10-position carousel filter holder. One 47 mm dia ammoniated filter from the 1-hour 50 mph cruise was used for XRF analyses. Ten elements were measured; bromine, lead, zinc, copper, iron, sulfur, calcium, phosphorus, aluminum, and manganese. The XRF system was calibrated with standards purchased from Columbia Scientific Industries. Multiple standards were used for each element from which a least squares calibration line was calculated. Correlation coefficients for these calibration lines were typically 0.999, indicating excellent linearity to the lower limit of detectability. Some additional calibrations were performed for light elements (sulfur, phosphorus, manganese) by deposition of aerosol particulate on fluoropore filters. These filters were analyzed both by XRF and atomic absorbtion to establish calibration.

Comparison of BCA, XRF and Ion Chromatograph Sulfate Methods --

To check the integrity of BCA sulfate results, the duplicate 50 mph cruise filters previously used for XRF elemental analysis were analyzed for sulfate by ion chromatography(23) at the end of the project. A valid comparison of sulfate values from simultaneously collected filters required an allowance for unav[illegible]

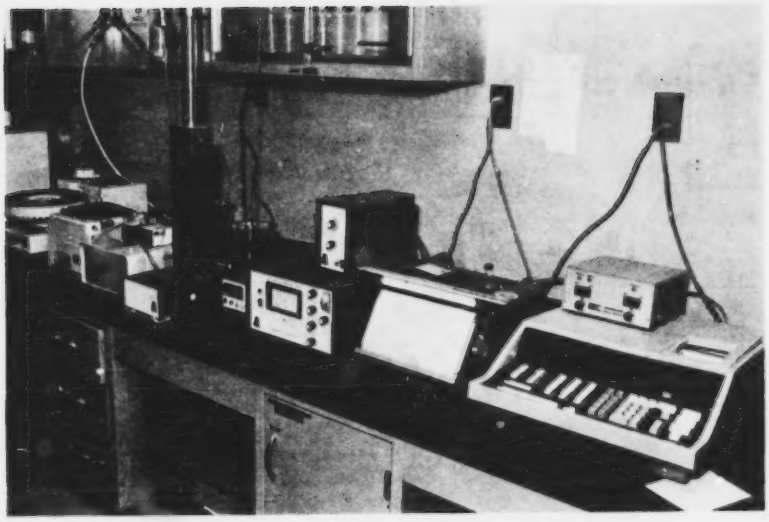


Figure 56. BCA Apparatus Set-Up.

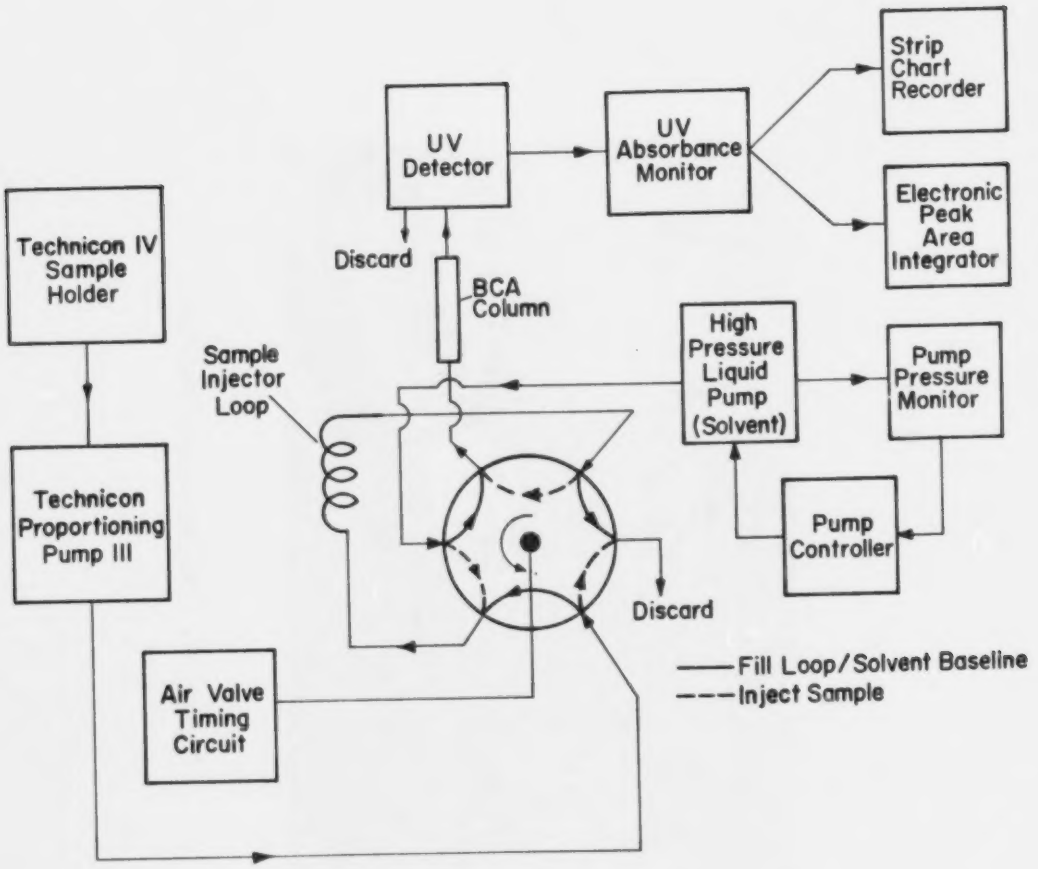


Figure 57
SCHEMATIC FOR AUTOMATED BARIUM CHLORANILATE SYSTEM

Figure 58. xrf System for Particulate Analysis.

able flow differences between the filter used for BCA analysis, and the XRF filter. An indication of differences between these filters can be seen in a comparison of specific total particulate loadings as illustrated by Figure 59. Most of the points far from the diagonal on Figure 59 represent cases where one or both of the filters plugged during the 50 mph cruise. These cases were not included in the pool of data used for BCA-IC comparisons.

Figure 60 illustrates the comparison of IC to BCA sulfate values for those tests where sulfate responses are above the detectable limit for both instruments and no filter plugging was encountered.

The same filter was used for elemental sulfur determination by XRF and sulfur in the form of sulfate by IC. A comparison of these results in Figure 61 indicate that essentially all sulfur on the filters was found as sulfate. For sulfur mass emission rates above 2 mg/mi, IC sulfur values were larger than those determined by XRF.

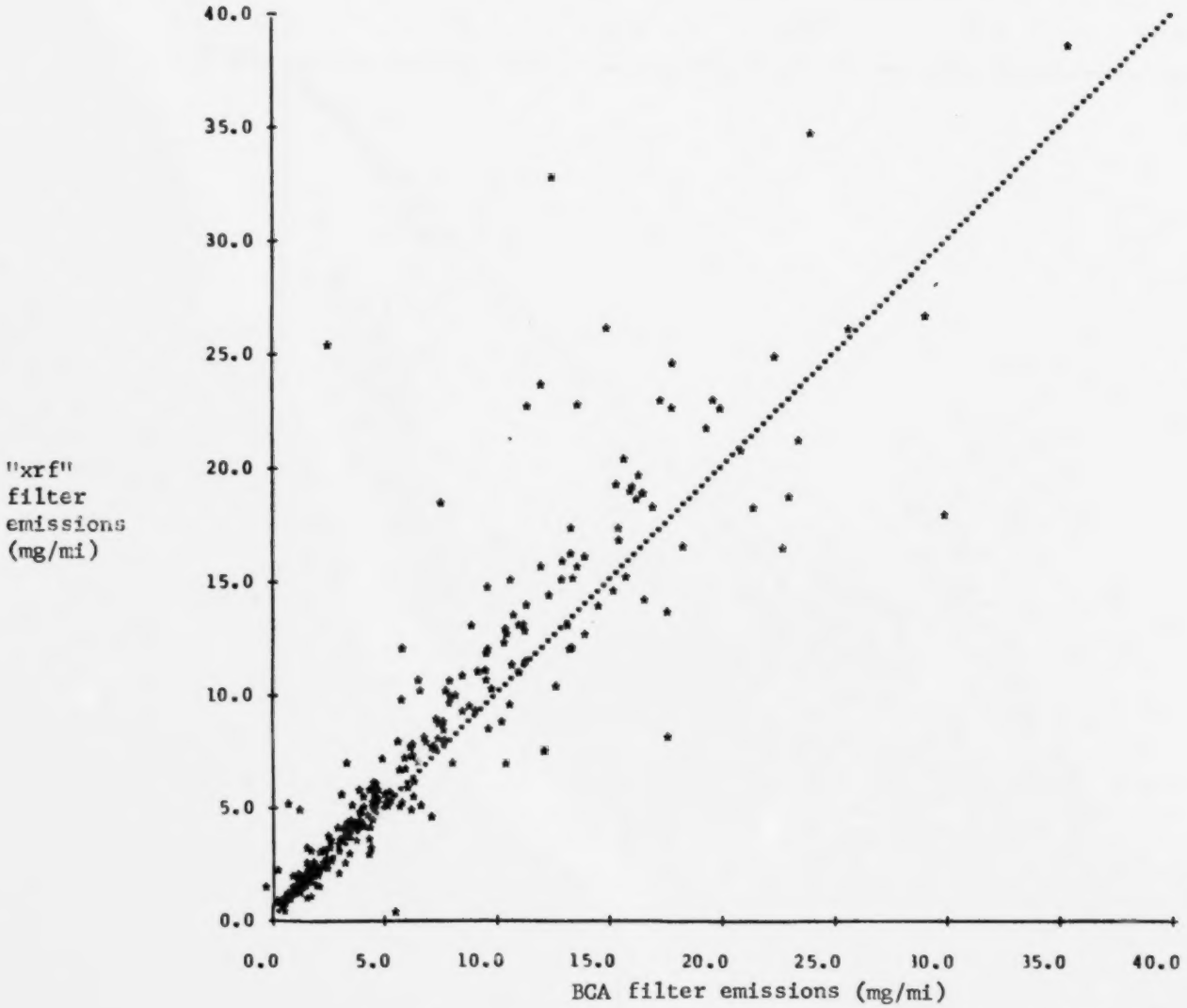


Figure 59. Comparison of Total Particulate Emissions for Two Probes.

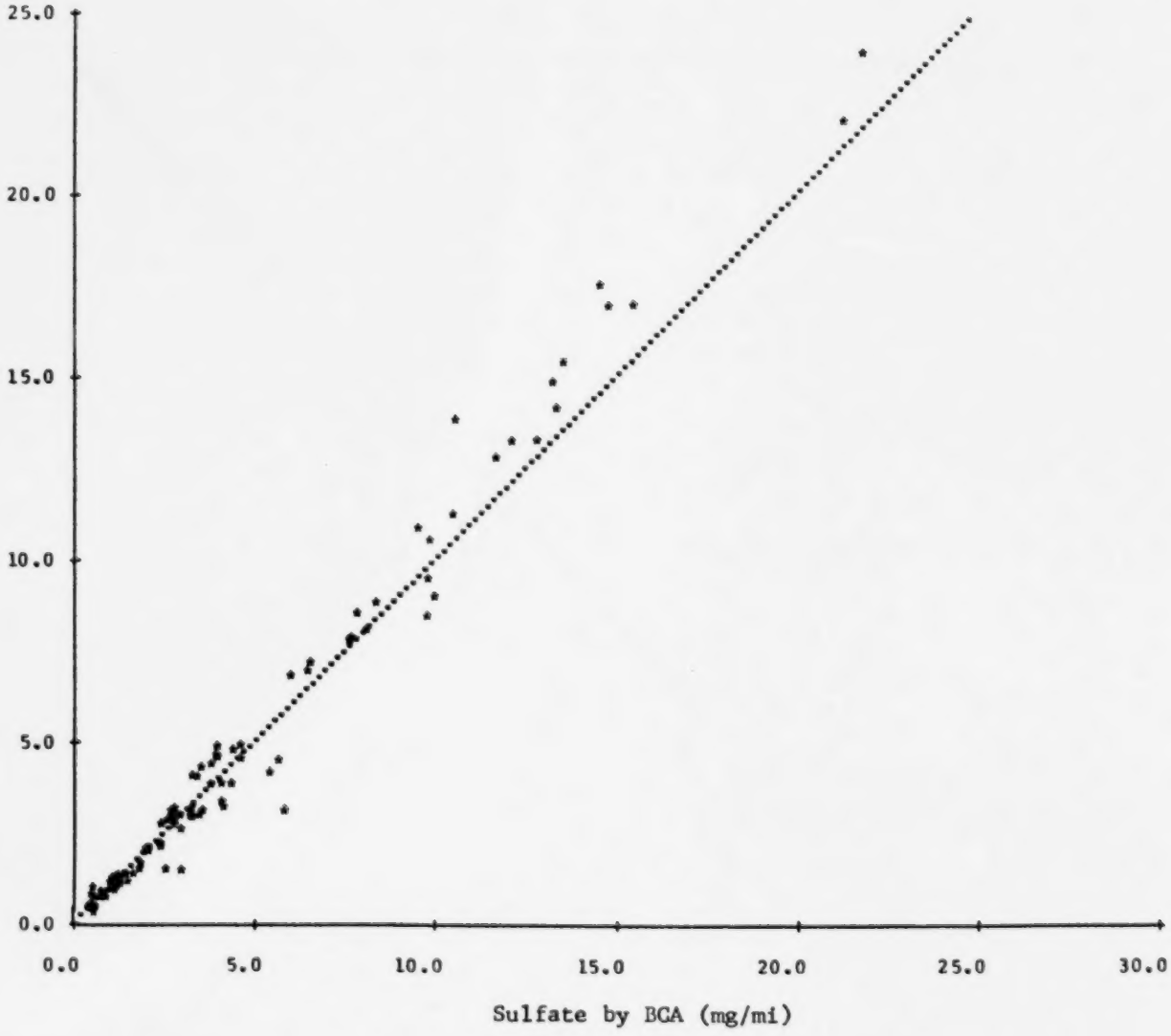


Figure 60. Comparison of IC and BCA Sulfate Analysis.

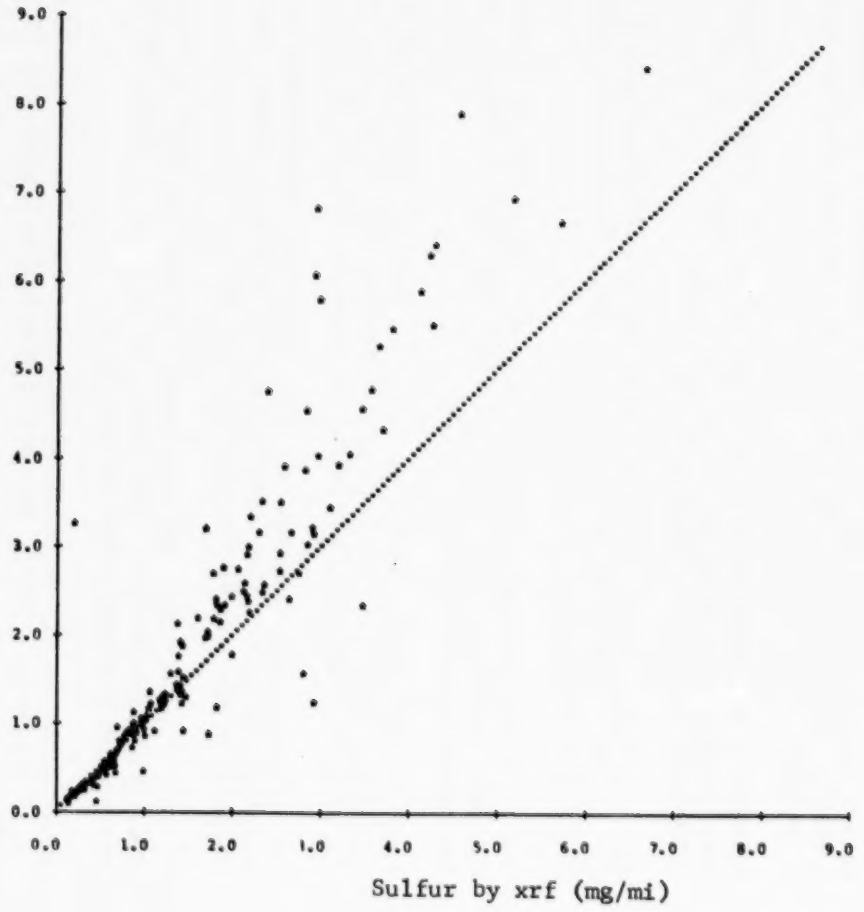


Figure 61. Comparison of IC and xrf Sulfur Analysis.

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APPENDIX A

A punched-tape computer output of the project data base has been provided to EPA. Request for copies of this tape should be directed to Mr. Peter Gabele, MD-46, MSERB, EMCD, ESRL, EPA, Research Triangle Park, North Carolina. Table 26 is a copy of a typical vehicle test output from the punched tape, and Table 27 defines the variable identifiers from Table 1.

TABLE 26

Computer Output for Typical Emissions Test

TEST	CAR	DATE	CAR YR	MAKE	MODEL	MILEAGE	HOURS	CALS
101	9	7/28/76	1975	PLYMOUTH	FURY	21530.0	364.8	830.3

		FTP		50-C	CFDS 1	CFDS 2
V-MIX	93.82	161.65	94.03	662.45	258.93	259.00
KH	0.90	0.90	0.92	0.92	0.92	0.92
DF	6.80	12.50	8.85	6.13	8.26	8.13
HC TG	16.82	8.85	5.67	4.95	9.06	9.29
CO TG	533.27	213.21	77.55	3.78	122.57	121.35
NOX TG	5.93	9.03	11.25	65.44	28.42	29.49
CO2 TG	2287.04	2459.58	2251.97	25172.17	6996.62	7106.48
HC G/M	2.58	0.00	0.00	0.09	0.67	0.69
CO G/M	64.90	0.00	0.00	0.07	9.08	8.99
NOX G/M	2.40	0.00	0.00	1.31	2.11	2.18
CO2 G/M	630.22	0.00	0.00	503.44	518.27	526.41
MPG	11.99	0.00	0.00	17.62	16.60	16.35

LAC 1 STALL 0

	CFDS 3	CFDS 4	CFDS 5	HFET
V-MIX	258.33	258.86	258.68	0.00
KH	0.92	0.92	0.91	0.00
DF	8.33	8.33	8.26	0.00
HC TG	9.46	9.58	9.65	0.00
CO TG	124.00	124.30	122.60	0.00
NOX TG	27.22	26.68	27.14	0.00
CO2 TG	6885.43	6902.10	7083.91	0.00
HC G/M	0.70	0.71	0.72	0.00
CO G/M	9.19	9.21	9.08	0.00
NOX G/M	2.02	1.98	2.01	0.00
CO2 G/M	510.03	511.27	524.73	0.00
MPG	16.65	16.81	16.40	0.00

	FTP	50C	CFDS 1	CFDS 2	CFDS 3	CFDS 4	CFDS 5	HFET
SO2 MG/M CYCLE	2.31	10.88	37.37	30.99	30.56	30.71	30.11	0.00
SO2 MG/M CYC.+ID	0.00	22.47	57.12	48.80	46.24	47.60	45.08	0.00
% FUEL S AS SO2	2.46	35.10	84.08	70.76	69.09	70.94	65.55	0.00
PART MASS MG/M	0.00	28.03	1.56	0.00	0.00	0.00	0.00	0.00
SO4 MG/M CYCLE	0.00	4.87	0.37	0.00	0.00	0.00	0.00	0.00
% FUEL S AS SO4	0.00	5.07	0.37	0.00	0.00	0.00	0.00	0.00

CHECK IN		FUEL		XRF MG/M	
CANIS	3.0	S % WT	0.020	MASS	15.857
IDLE SPD	650.0	PB G/GAL	0.007	BR	0.007
IDLE TIM	1.0	P G/GAL	0.000	PB	0.012
IDLE HC	200.0	R.V.P.	9.400	ZN	0.030
IDLE CO	7.0	A.P.I.	58.400	CL	0.000
SP MIN	6.0	DENSITY	0.745	FE	0.000
SP MAX	10.0	I.B.P	89.000	S	1.406
1000 HC	120.0	10 %	123.000	CA	0.017
1000 CO	3.0	50 %	221.000	P	0.016
FULL ADV	39.0	90 %	355.000	AL	0.000
HISPD HC	120.0	EP	404.000	MN	0.000
HISPD CO	0.0	MN G/GAL	0.000		

TABLE 27

Computer Output Parameter List

Item	Description
Test	Serial number of test
Car	Test group vehicle number
Date	Date of test
Mileage	Odometer at date of test
Hours	Reading from under-hood hour meter } zero values indicate
Gals	Reading from under-hood fuel meter } missing data
V-MIX	CVS v-mix (m^3)
KH	Humidity correction factor
DF	Dilution factor
HC TG	Total grams from particular test segment
CO TG	" " " " " "
NO_x TG	" " " " " "
CO_2 TG	" " " " " "
HC G/M	Emission rate gm/mi
CO G/M	" " "
NO_x G/M	" " "
CO_2 G/M	" " "
MPG	Carbon balance fuel economy
SO_2 MG/M Cycle	SO_2 Emissions rate (mg/mi) - cycle only
SO_2 MG/M Cycle + ID	SO_2 Emission rate (mg/mi) - cycle + idle purge
% Fuel S as SO_2	% Fuel sulfur emitted as SO_2, includes idle purge
Part MASS MG/M	Total Particulate emission, gravimetric (mg/mi)
SO_4 MG/M Cycle	Sulfate emission by BCA (mg/mi)
% Fuel S as SO_4	% Fuel Sulfur emitted as sulfate
OWNER	Identifies vehicle source: 0 = AEL, 1 = Red Cross, 2 = NYS Thruway, 3 = NYS Office of General Services, 4 = NY Telephone Co., 5 = Private
IDLE SPD	Vehicle idle speed
IDLE TIM	Spark advance BTDC, negative values indicate retard
IDLE HC	HC concentration at idle, ppm hexane
IDLE CO	CO concentration at idle (%)
SP MIN	Lowest spark firing voltage (K volts)
SP MAX	Highest spark firing voltage (K volts)
1000 HC	HC concentration at 1000 rpm
1000 CO	CO concentration at 1000 rpm
FULL ADV	Spark advance at 2500 rpm minus initial advance
HISPD HC	HC concentration at 2500 rpm, ppm hexane
HISPD CO	CO concentration at 2500 rpm, %

TABLE 27
(continued)

Computer Output Parameter List

Item	Description
S % WT	Sulfur content wt %
PB	Lead content gm/gal
P	Phosphorous content gm/gal
R.V.P.	Reid Vapor Pressure (lb)
A.P.I.	API gravity at 60°F
DENSITY	Density at 15°C (gm/cm^3)
IBP	Distillation Analysis (°F)
10%	" "
50%	" "
90%	" "
EP	" "
MN	Manganese content (gm/gal)
MASS	Total particulate emission rate for xrf filter (mg/mi)
Br, Pb, etc.	Emission rate (mg/mi)

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